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VOLUME XXXI

NUMBER FOUR

# RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED IN FIVE ISSUES BY THE  
DIVISION OF RUBBER CHEMISTRY  
OF THE AMERICAN CHEMICAL SOCIETY





# KOSMOS 60

Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil, and its manufacture is scientifically controlled to meet the highest standards. Its superb processing and balance of strength make for the best in rubber products.

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Philblack A, Fast Extrusion Furnace Black. Excellent tubing, molding, calendering, finish! Mixes easily. Disperses heat. Non-staining.



Philblack O, High Abrasion Furnace Black. For long, durable life. Good conductivity. Excellent flex life and hot tensile. Easy processing.



Philblack I, Intermediate Super Abrasion Furnace Black. Superior abrasion. More tread miles at moderate cost.



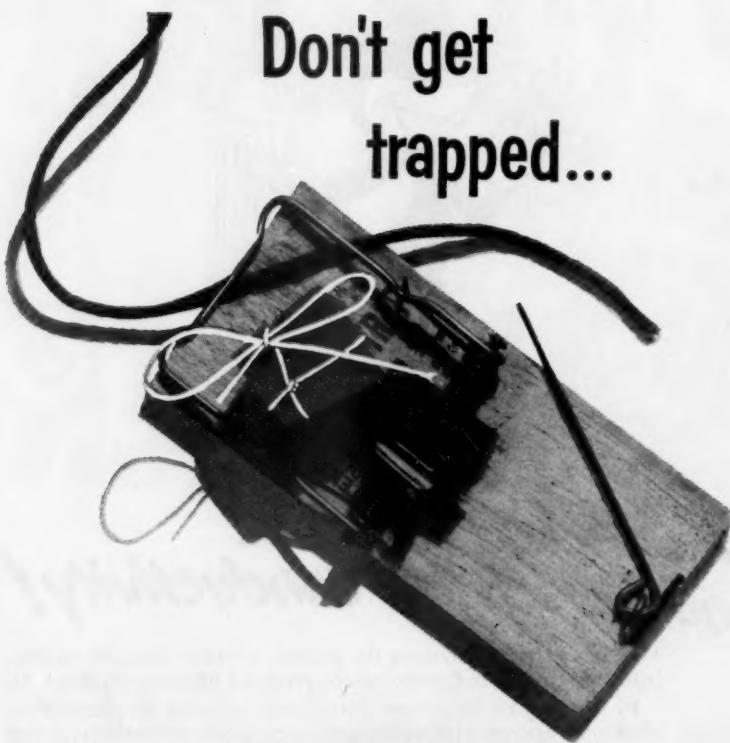
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District Offices: Chicago, Dallas, Providence and Trenton • West Coast: Harwick Standard Chemical Company, Los Angeles, California • Warehouse Stocks at Akron, Chicago, Trenton, Brighton, Mass. and Toronto, Canada • Export Sales: 80 Broadway, New York 5, New York • European Office: Phillips Chemical Company, Limmatquai 70, Zurich 1, Switzerland.

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. and R. of 1948, authorized September 25, 1940.

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by inferior carbon blacks—  
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blacks in your natural and synthetic  
rubber formulations. Highest manufacturing  
standards guarantee uniformity and economy...  
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**FOR CRACKING CONTROL**

YOU CAN ENHANCE SALABILITY OF YOUR  
RUBBER PRODUCTS BY PROVIDING THEM COMPLETE  
PROTECTION FROM OZONE CRACKING WITH  
UNIVERSAL'S ANTIOZONANTS UOP 88 AND UOP 288

If your product is made of rubber, either natural or synthetic, you should protect it from ozone. With UOP 88 and the newer UOP 288 you can completely eliminate ozone cracking. Don't take chances with the salability of your product when it comes face to face with the potential customer. Don't jeopardize repeat business with merchandise that cracks and deteriorates. Use UOP 88 or UOP 288—premium antiozonants for superior products. Write us for details.



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PRODUCTS COMPANY**

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# DU PONT

# CHEMICALS and

# COLORS

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**DEPENDABLE IN PERFORMANCE . . . UNIFORM IN QUALITY**

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Accelerator 552	NA-22	Thiuram E Grains
Accelerator 808	Permalux	Thiuram M
Accelerator 833	Polyac Pellets	Thiuram M Grains
Conac S	Tepridone	Zenite
MBT	Tetrone A	Zenite Special
MBTS	Thionex	Zenite A
	Thionex Grains	Zenite AM

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Hylene® M-50	Hylene® TM
Hylene® MP	Hylene® TM-65

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Akroflex CD Pellets	Neozone D	Zalba
Antox	Permalux	

### PEPTIZING AGENTS

Endor	RPA No. 3 Concentrated
	RPA No. 6
RPA No. 3	RR-10

### RECLAIMING CHEMICALS

RPA No. 3	RR-10
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### AQUAREXES (MOLD LUBRICANTS AND DISPERSING AGENTS)

Aquarex D	Aquarex MDL	Aquarex SMO
Aquarex G	Aquarex ME	Aquarex WAQ
Aquarex L	Aquarex NS	

### BLOWING AGENTS

Unicel ND	Unicel NDX	Unicel S
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### COLORS—Rubber Dispersed Colors

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Rubber Red 2BD	Rubber Blue PCD
Rubber Yellow GD	Rubber Blue GD
Rubber Green GSD	Rubber Orange OD

### SPECIAL-PURPOSE CHEMICALS

**BARAK**—Retarder activator for thiazole accelerators

**Copper Inhibitor 85**—Inhibits catalytic action of copper on elastomers

**ELA, ELA-N**—Elastomer lubricating agents

**HELIOZONE**—Sun-checking inhibitor

**NBC**—Inhibits weather and ozone cracking of SBR compounds. Improves heat and sunlight discoloration resistance of neoprene stocks.

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Retarder-activator for acidic accelerators. Also an activator for certain blowing agents.

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In Canada contact: DuPont Company of Canada (1956) Ltd., Box 640, Montreal

E. I. du Pont de Nemours & Co. (Inc.)  
**Elastomer Chemicals Department**



**Better Things for Better Living**  
... through Chemistry

### MILL SHRINKAGE TEST

(Stock placed on cold mill, preset at .050" between rolls. After stock warmed,  
samples cut and permitted to cool)

<b>HARDNESS:</b>  80 DUROMETER					
					
 40 DUROMETER					
	0% CHEMIGUM N-8  100% Polymer "A"	25% CHEMIGUM N-8  75% Polymer "A"	50% CHEMIGUM N-8  50% Polymer "A"	75% CHEMIGUM N-8  25% Polymer "A"	100% CHEMIGUM N-8  0% Polymer "A"
<b>STOCK COMPOSITION:</b>					

### How to improve the run of your mill

The samples above tell the story. Taken from a series of test mill runs, they graphically illustrate the superior processability of new CHEMIGUM N-8 and how it can be used to improve the processing of other nitrile rubbers.

CHEMIGUM N-8 is an intermediate acrylonitrile content copolymer and exhibits corresponding oil resistance and physical properties. It also exhibits very rapid mill breakdown and will form a smooth sheet immediately, even on a cold mill.

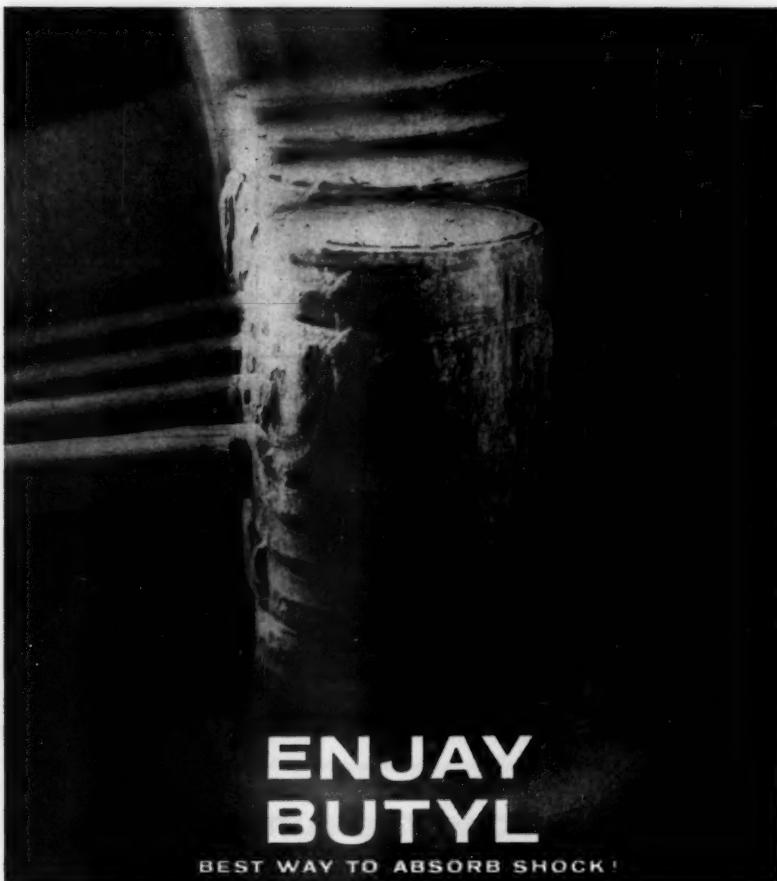
By blending CHEMIGUM N-8 with other nitrile, styrene or natural rubbers, processing characteristics and physical properties can be obtained which previously were not possible. And, since it is stabilized with a nonstaining, non-discoloring antioxidant, it can be used in the most exacting color applications. For full details on unusual CHEMIGUM N-8, including the latest *Tech Book Bulletins*, just write to Goodyear, Chemical Division, Dept. V-9430, Akron 16, Ohio.



# GOOD YEAR

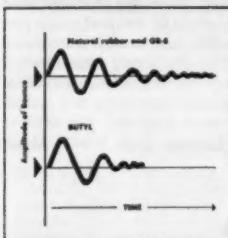
CHEMICAL DIVISION

CHEMIGUM—T.M. The Goodyear Tire & Rubber Company, Akron, Ohio



# ENJAY BUTYL

BEST WAY TO ABSORB SHOCK!



Butyl's superior shock-absorption characteristics reduce amplitude of bounce in much less time as compared with other rubbers.

Enjay Butyl, because of its higher damping factor, absorbs shock energy *more completely* than any other rubber. Through simple variations in compounding or processing, you can build the right degree of resiliency for your requirements. Butyl is the ideal rubber for motor mounts, load cushions, sound deadener insulation, axle and body bumpers—and other shock, noise and mechanical-vibration applications.

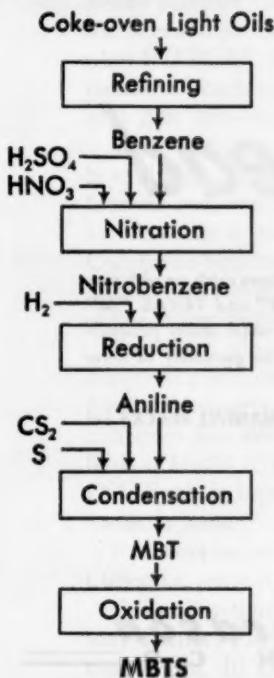
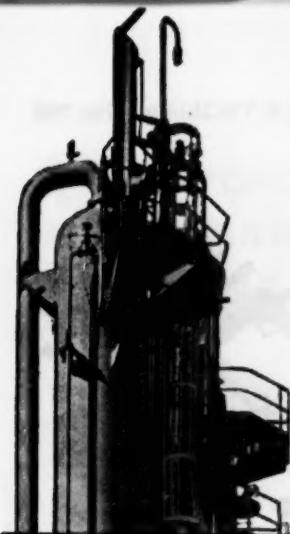
Butyl *also* offers outstanding resistance to weathering and sunlight . . . chemicals . . . heat . . . abrasion, tear and flexing . . . unmatched electrical properties and impermeability to gases and moisture.

Find out how this versatile rubber can improve your product. Call or write the Enjay Company, today!



Pioneer in Petrochemicals

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Akron • Boston • Charlotte • Chicago • Detroit • Los Angeles • New Orleans • Tulsa



Starting from coke-oven Light Oils, Cyanamid performs and controls each step to the final product...MBTS.

*If you want the best—buy  
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Cyanamid  
is basic  
in the  
production  
of  
**MBTS**



*... stay ahead*

It's too late when your competitors catch up with you.  
Stay ahead with **TEXAS "E"** and **TEXAS "M"**  
**CHANNEL BLACKS**. They offer many product-improving opportunities plus the possibility of lower compound costs.

The plus margins in **TEXAS CHANNEL BLACKS** can help you stay ahead.



**Sid Richardson**  
CARBON CO.

FORT WORTH, TEXAS

GENERAL SALES OFFICES  
EVANS BUILDING  
AKRON, OHIO

**REINFORCED WITH HI-SIL® 233,  
RESILIENT \*RIPPLE® SOLE  
REGISTERS RESOUNDING RECEPTION**



RIPPLE® Soles, as displayed on these shoes by (left to right) Cardone & Baker, E. T. Wright, and Buster Brown, are available in red, chocolate, natural, grey, black and white.

\*TM—RIPPLE SOLE CORP.

Beebe Rubber Company of Nashua, New Hampshire, is the licensed producer of the unique and increasingly popular RIPPLE® Sole. Compound requirements are extreme; a combination of singularly good abrasion, tear, and flex life—with outstanding bounce and resilience.

The "Vees" molded into the RIPPLE® Sole must rebound from rough and rugged treatment, since only the limited area of their crowns constitutes the entire walking surface. It's a job of reinforcement tailor-made for our Columbia-Southern Hi-Sil 233, which in Beebe's judgment "just works out better in our compounds than any of the other reinforcers we'd tried."

Excellent physicals in brightly colored stocks are no longer a problem, with Columbia-Southern white reinforcing pigments on the scene. If spectrum-spanning color can give *your* compounds a lift, we suggest you take a look at Hi-Sil 233, Silene® EF, or Calcene® TM, NC, or CO. Each is tops in its field . . . and *should* be in your formula book.

For working samples, contact our nearest District Sales Office or write direct to Room 1929T at Pittsburgh.

Columbia-Southern Chemical Corporation, One Gateway Center, Pittsburgh 22, Pa. Offices in fourteen principal cities. In Canada: Standard Chemical Limited.

**COLUMBIA-SOUTHERN  
CHEMICAL CORPORATION**

A Subsidiary of Pittsburgh Plate Glass Company

# MONSANTO RUBBER CHEMICALS ANSWER A FREQUENTLY ASKED COMPOUNDING QUESTION

**QUESTION:** *What new, solid antiozonant guards rubber against ozone cracking with minimum staining ???*

**ANSWER:**

*New Santoflex GP*

Monsanto announces Santoflex GP—the newest and best antiozonant you can use to "vaccinate" rubber against ozone attack. "GP" shows minimum staining. Now you can benefit from an antiozonant in mechanical goods and other industrial products just as tire-makers do in their compounds...Santoflex GP gives prolonged crack resistance to belting, electrical insulation, motor mounts, hose and appliance parts. An easily handled solid, "GP" imparts excellent ozone resistance.

Static Ozone Test (48 Hours)



Dynamic Ozone Test (36,000 Flexes—48 Hours)



Migration Stain Test



(ASTM Test D-925-55, Method B)

See the difference 2-PPH Santoflex GP makes on SBR-1500 in a typical compound. Stocks exposed to approximately 50 parts of ozone per 100 million parts of air at 100°F. for 48 hours show how Santoflex GP substantially retards ozone cracking—yet they show only slight staining of a white auto lacquer.

**SEND COUPON FOR SAMPLES...TECHNICAL HELP** Every application, plant and process has different compound requirements. That's why Monsanto recommends no "canned" formulations or "cure-all's"—we do offer samples of Santoflex GP along with technical help in testing it out for your specific application. The coupon is for your convenience.

SANTOFLEX: MONSANTO T. M., REG. U. S. PAT. OFF.



MONSANTO CHEMICAL COMPANY  
Rubber Chemicals Department, Akron 11, Ohio

Please send me a sample of new Santoflex GP.

NAME.....

COMPANY.....

ADDRESS.....

CITY.....

ZONE..... STATE.....



*Philprene\* rubber  
for low water absorption!*

CURRENT PHILPRENE POLYMERS

	NON-PIGMENTED	PIGMENTED WITH PHILBLACK*
<b>HOT</b>	PHILPRENE 1000	
	PHILPRENE 1001	PHILPRENE 1100 **
	PHILPRENE 1006	PHILPRENE 1104
	PHILPRENE 1009	
	PHILPRENE 1010	** Pigmented with EPC Black
	PHILPRENE 1018	
	PHILPRENE 1019	
<b>COLD</b>	PHILPRENE 1500	PHILPRENE 1601
	PHILPRENE 1502	PHILPRENE 1605
	PHILPRENE 1503	
<b>COLD OIL</b>	PHILPRENE 1703	PHILPRENE 1803
	PHILPRENE 1706	PHILPRENE 1805
	PHILPRENE 1708	
	PHILPRENE 1712	

Let it rain! Water is no problem with Philprene 1018. Used with other polymers, Philprene 1018 provides protection against water . . . for wire and cable jackets, rubber footwear, storm coats and other rubber articles.

Phillips Chemical Company makes the largest variety of commercially available polymers on the market. You can select one that is practically made to your specifications! Consult your Phillips technical representative for complete information.

\*A trademark



PHILLIPS CHEMICAL COMPANY, Rubber Chemicals Division, 318 Water Street, Akron 8, Ohio  
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<b>CHANNEL BLACKS:</b> Spheron 9 EPC	Spheron 6 MPC	Spheron C CC
<b>FURNACE BLACKS:</b> Vulcan 9 SAF	Vulcan 6 ISAF	Vulcan 3 HAF      Vulcan XC-72 ECF
Vulcan SC SCF	Vulcan C CF	Sterling SO FEF      Sterling V GPF
Sterling L HMF	Sterling LL HMF	Sterling NS SRF      Pelletex SRF
Pelletex NS SRF	Sterling R SRF	Gastex SRF
<b>THERMAL BLACKS:</b> Sterling FT	Sterling MT	Sterling MT-NS

*Free Samples, Technical Literature Available*

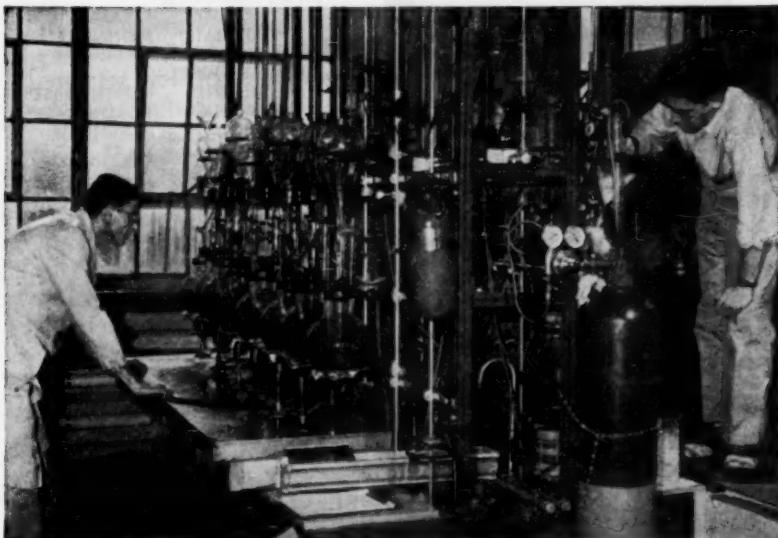


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New, Additional Research and  
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THIOKOL CHEMICAL CORPORATION

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for its liquid polymers, rocket propellants, plasticizers  
and other chemical products.

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**TRY  
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NAUGATUCK supplies a complete line of proven accelerators, activators, anti-oxidants, and special chemicals to give you thorough control of rubber product manufacture and performance.

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M-B-T-S	
THIURAMS —	
MONEX*†	TUETX†
MORFEX	ETHYL TUETX†
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XANTHATES —	
C-P-B*	Z-B-X*

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D-B-A	G-M-F

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DDM — modifier	
THIOSTOP K&N — short stops	
POLYGARD — stabilizer	Reg. U. S. Pat. Off.

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- Reclaimed Rubber
- Synthetic Rubber
- Latices

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**Naugatuck Chemical**

Division of United States Rubber Company

Naugatuck, Connecticut



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# Naugatuck NAUGAPOL<sup>S</sup>

*answer your  
problems in.....*

For products requiring excellent electrical properties and for those items designed for low moisture absorption, NAUGAPOL, butadiene-styrene copolymers, "Specially Processed" during the finishing operation, is the best obtainable.

R-S RUBBER  
ELECTRICAL  
INSULATION

#### Current NAUGAPOL Polymers for electrical applications

##### HOT TYPES

GRADE	CLASS	END USES
NAUGAPOL 1016	Staining	Standard grade for wire and cable and mechanical goods.
NAUGAPOL 1018	Non-staining	Crosslinked processing aid. Wire and cable and mechanical goods.
NAUGAPOL 1019	Non-staining	Standard grade for wire and cable and mechanical goods.
NAUGAPOL 1023	Staining	Low styrene content. Wire and cable and mechanical goods for arctic service.

##### COLD TYPES

GRADE	CLASS	END USES
NAUGAPOL 1503	Non-staining	Standard grade for wire and cable and mechanical goods.
NAUGAPOL 1504	Non-staining	Low styrene content. Wire and cable and mechanical goods for arctic service.

For technical data, information or assistance that will help you in processing of your rubber compounds, write to us on your company letterhead.



## Naugatuck Chemical

Division of United States Rubber Company  
Naugatuck, Connecticut

IN CANADA: NAUGATUCK CHEMICALS, Elmsira, Ontario • Cable Address: Rubexport, N.Y.  
Rubber Chemicals • Synthetic Rubber • Plastics • Agricultural Chemicals • Reclaimed Rubber • Latices



# HOW YOU BENEFIT WHEN YOU USE SUN RUBBER PROCESS AIDS

<b>IF YOU PROCESS</b>	<b>USE</b>	<b>BECAUSE</b>
OIL EXTENDED POLYMERS GR-S TYPES 1703 1707 1708 1801	<b>CIRCOSOL-2XH</b>	New low cost! Low staining properties on white goods. Improves GR-S rebound. Constant uniformity assures minimum down-grading.
OIL EXTENDED POLYMERS GR-S TYPES 1705 1709 1710	<b>SUNDEX-53</b>	Versatile. Highly compatible with natural rubber, re-claims, GR-S types.
NEOPRENE WHV	<b>SUNDEX-53</b>	Cost of compounds comparable to low-cost elastomers.
REGULAR NEOPRENES and NATURAL RUBBER	<b>CIRCO LIGHT RUBBER PROCESS-AID</b>	True softening by physical changes in rubber structure. Large quantities absorbed without blooming.

To learn more about using Sun Rubber Process Aids to get better physicals, lower costs, and easier processing, see your Sun representative. Or write for your copy of Sun's latest Technical Bulletin describing any of the above products. Address SUN OIL COMPANY, Philadelphia 3, Pa., Dept. RC-4.

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# SUN OIL COMPANY

PHILADELPHIA 3, PA.



IN CANADA: SUN OIL COMPANY, LTD., TORONTO AND MONTREAL

OCTOBER - NOVEMBER • 1958

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PUBLISHED IN FIVE ISSUES BY THE  
DIVISION OF RUBBER CHEMISTRY  
OF THE AMERICAN CHEMICAL SOCIETY



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*for RUBBER COMPOUNDING*

**STATEX®-160 SAF** (Super Abrasion Furnace)

**STATEX®-125 ISAF**

(Intermediate Super Abrasion Furnace)

**STATEX-R HAF** (High Abrasion Furnace)

**STANDARD MICRONEX® MPC**

(Medium Processing Channel)

**MICRONEX W-6 EPC** (Easy Processing Channel)

**STATEX-B FF** (Fine Furnace)

**STATEX-M FEF** (Fast Extruding Furnace)

**STATEX-93 HMF** (High Modulus Furnace)

**STATEX-G GPF** (General Purpose Furnace)

**FURNEX® SRF** (Semi-Reinforcing Furnace)

\* COLUMBIAN COLLOIDS \*

## COLUMBIAN CARBON COMPANY

380 Madison Ave.



New York 17, N.Y.

# RUBBER CHEMISTRY AND TECHNOLOGY

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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. One object of the publication is to render available in convenient form under one cover important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances. Another object is to publish timely reviews.

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### **CHARLES GOODYEAR MEDAL AWARD FOR 1959**

To all members of the Division of Rubber Chemistry:

This letter is for the purpose of soliciting proposals for candidates for the Charles Goodyear Medal Award for consideration by the Medal Committee at the Spring meeting to be held in Los Angeles, May 12-15, 1959.

Your proposals should be presented in the form suggested in the *Outline for Proposal* given below, and mailed to the Division Secretary, Dr. R. H. Gerke, so as to reach him not later than April 1.

For your guidance, I am listing below the past Goodyear Medalists and also a list of fields not yet fully recognized. Additional awards in fields already recognized, e.g., polymerization and vulcanization, are, of course, in order. The by-laws do not prohibit the election of a foreign technologist.

I hope that each of you will consider this matter carefully.

R. F. Dunbrook, Chairman  
Charles Goodyear Medal Committee

### **OUTLINE FOR PROPOSAL OF A CANDIDATE**

#### **FOR THE CHARLES GOODYEAR MEDAL AWARD**

1. Name of candidate . . . . .
2. Statement of contribution of candidate for use for the Award Citation . . . . .
3. General statement concerning the importance of such contribution . . . . .
4. Pertinent publications of the candidate . . . . .
5. Brief biography of the candidate . . . . .
6. Name, address, and signature of proposer member of the Division of Rubber Chemistry

## FIELDS NOT YET FULLY RECOGNIZED

Among fields which have not been fully recognized may be mentioned: Physics of rubber, including kinetic theory, dynamic and electrical properties; reinforcement; oxidation; antioxidants; polychloroprene (neoprene); vulcanizable copolymers of isobutylene and dienes (butyl); cold SBR and oil-extended SBR; polyacrylate rubbers; silicone rubbers; isocyanate rubbers; reclaiming; delayed-action accelerators; new reinforcing fillers; new processing equipment.

## CHARLES GOODYEAR MEDALISTS

- 1941 DAVID SPENCE. A pioneer of rubber chemistry, who did much important early work. No lecture given.
- 1942 L. B. SEBRELL. Research on antioxidants and accelerators. Lecture: "The Second Mile", *Industrial and Engineering Chemistry*, 1943, p. 736; *RUBBER CHEMISTRY AND TECHNOLOGY*, 1943, p. 713.
- 1944 W. L. SEMON. Synthetic rubber research. Lecture: "Research leading to commercial butadiene synthetic rubber", *Chemical and Engineering News*, 1946, p. 2900; *India Rubber World*, 1946, p. 364.
- 1946 IRA WILLIAMS. Neoprene and overall accomplishments. Lecture: "Vulcanization of rubber with sulfur", *Industrial and Engineering Chemistry*, 1947, p. 901.
- 1948 GEORGE OENSLAGER. Pioneer in organic accelerators. No lecture given.
- 1949 H. L. FISHER. Long in the field of rubber chemistry; overall accomplishments. Lecture: "Rubber research and the need for a rubber research institute in the United States".
- 1950 C. C. DAVIS. Development of the oxygen bomb test for accelerated aging; *Chemical Abstracts*; *RUBBER CHEMISTRY AND TECHNOLOGY*; Editor "The Chemistry and Technology of Rubber". Lecture: "Some of the real pioneers of the rubber industry", *India Rubber World*, 1951, p. 433.
- 1951 W. C. GEER. Oven aging test, de-icer for airplanes, encouragement of rubber research. Lecture: "Strategy in rubber research", *Industrial and Engineering Chemistry*, 1951, p. 2436.
- 1952 H. E. SIMMONS. One of the early and best known teachers of rubber chemistry, and an inspirational guidance of younger men. Lecture: "Out of the past".
- 1953 J. T. BLAKE. Research on oxidation and vulcanization. Co-editor of "The Chemistry and Technology of Rubber". Accumulative accomplishments. Lecture: "The future of rubber", *Chemical and Engineering News*, 1953, p. 4290.
- 1954 G. S. WHITBY. Research on plantation rubber, vulcanization, accelerators, GR-S synthesis, overall accomplishments. Editor of "Synthetic Rubber". Lecture "Reflections on rubber research", *Industrial and Engineering Chemistry*, 1955, p. 806.
- 1955 R. P. DINSMORE. Numerous important contributions to rubber chemistry and technology; recipient of honors. Lecture: "Specifications for a rubber chemist", *Rubber World*, 1956, p. 57.
- 1956 S. M. CADWELL. Contributions to the field of rubber chemicals and to the control of vulcanization. Lecture: "Scientific Contributions to the Rubber Industry".

- 1957 A. W. CARPENTER. For his many contributions to the testing of rubber and rubber products. Lecture: "The Tower of Babel", *Rubber World*, 1957, p. 241.
- 1958 J. C. PATRICK. For the discovery, development and vulcanization of Thiokol polysulfide polymers. Lecture: "Comments on the Polysulfide Polymers".

## FUTURE MEETINGS

Meeting		City	Hotel	Date
1959	Spring	Los Angeles	Biltmore	May 12-15
1959	Fall	Washington*	Shoreham	November 9-13
1960	Spring	Buffalo	Statler	May 3-6
1960	Fall	New York	Commodore	September 13-16
1961	Spring	Louisville	Brown	May 18-21
1961	Fall	Chicago	Sherman	September 5-8
1962	Spring	Boston	Statler	May 15-18
1962	Fall	Atlantic City, N. J.	Chalfonte	September 11-14

\* An international meeting jointly sponsored by the Division of Rubber Chemistry ACS, Committee D-11 of ASTM, and the Rubber and Plastics Division of ASME.

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1958

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*Chairman:* EARL R. BARTHOLOMEW (Wright-Patterson A. F. Base, Ohio).  
*Chairman Elect:* RUSSELL J. HOSKIN (Inland Mfg. Division, G. M. C., Dayton).  
*Secretary:* RAYMOND WELLS (Precision Rubber Products Corp., Dayton).  
*Treasurer:* DAYLE R. BUCHANAN (Inland Mfg. Division, G. M. C., Dayton).  
*Directors:* Three-Year Term: FRANK E. BELL, JR., WILLIAM L. NOLAN, REUBEN WOLK. Two-Year Term: JAMES L. FITZGERALD, FREDERICK W. GAGE, MAURICE LOWMAN. Meetings in 1958: October 9 and December 13. Outing in Dayton, June 7.

### SOUTHERN RUBBER GROUP

*Chairman:* THOMAS R. BROWN (The B. F. Goodrich Co., Tuscaloosa).  
*Vice-Chairman:* WARREN S. HALL (Phillips Chemical Co., Memphis 17, Tenn.).  
*Treasurer:* MONROE MIRSKY (Guiberson Corporation, Dallas). *Secretary:* ROGER B. PFAU (The C. P. Hall Co., Memphis). *Directors:* One-Year Term: JOHN R. GALLOWAY, ROBERT W. RICE, JOHN M. BOLT. Two-Year Term: ROBERT D. BAKER, ALBERT KOPER. Meetings in 1958: February 21, June 13, October 17 and (January 30, 1959).

### WASHINGTON RUBBER GROUP

*President:* DOUGLAS K. BONN (U. S. Rubber Co., Washington, D. C.).  
*Vice-President:* ROBERT D. STIEHLER (National Bureau of Standards, Washington, D. C.). *Secretary:* ARTHUR W. SLOAN (812 N. Fairfax Street, Alexandria, Va.). *Treasurer:* GEORGE W. FLANAGAN (B. F. Goodrich Chemical Co., Washington, D. C.). Term ends June 30, 1958. Meetings in 1958: January 15, February 18, April 16, May 21.

## 74TH MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY, SEPTEMBER 10-12, 1958

### SHERMAN HOTEL, CHICAGO, ILLINOIS

RAYMOND F. DUNBROOK, *Chairman*; ROSCOE H. GERKE, *Secretary*

### TECHNICAL PROGRAM

#### GENERAL PAPERS: ANALYTICAL, PIGMENTS AND PROPERTIES

R. F. DUNBROOK, *Presiding*

1. R. F. DUNBROOK, Introductory Remarks.
2. M. P. WAGNER, S. H. LANING, and J. W. SELLERS. The Determination of Zinc Oxide in Rubber Vulcanizates by X-Ray Diffraction.
3. ROGER W. STRASSBURG. Semi-Micro Determination of Free Sulfur in Cured Rubber Stocks.
4. R. A. HIVELY, and C. W. WADELIN. The Determination of Free Sulfur in Accelerators.
5. F. B. SMITH, and W. F. TULEY. Accelerated Testing of Ozone Cracking Inhibitors.

6. J. S. LOWE, and J. A. CARR. The Formation of Volatile Fatty Acids in Ammonia Preserved Natural Latex Concentrate.
7. B. A. HUNTER, A. C. NAWAKOWSKI, R. R. BARNHART, E. B. HANSEN, and E. M. CAMPBELL. Important Quality Factors in Styrene-Butadiene Rubber (SBR) as Affected by Stabilizers and Flocculation Technique.
8. MELVIN P. WAGNER, and JOHN W. SELLERS. Kinetics of Filler-Polymer Interaction Between Fine Particle Silica, or HAF Carbon Black and SBR or Butyl Rubber.
9. J. V. HALLUM, and H. V. DRUSHEL. The Organic Nature of Carbon Black Surfaces. II. Quinones and Hydroquinones by Coulometry at Controlled Potential.
10. PAUL FUGASSI, and GEORGE OSTAPCHENKO. The Sorption of Benzene by Natural and Synthetic Polymeric Hydrocarbons.

#### GENERAL PAPERS: VULCANIZATION AND DETERIORATION

E. H. KRISMANN, *Presiding*

11. DALE J. HARMON. Radiation Vulcanization of Elastomers.
12. G. E. MEYER, F. J. NAPLES, and H. M. RICE. Heat, Ozone, and Gamma Radiation Stability of Highly Saturated Adduct Rubber Vulcanizates.
13. F. M. O'CONNOR, and T. L. THOMAS. Chemical Loaded Molecular Sieves as Latent Curing Aids. II. Accelerators for Vulcanization of Neoprene.
14. ROGER E. KNOX. Molding of Resilient Urethane Foams.
15. E. M. BEVILACQUA. Degradation of Polyisoprene Networks by Oxygen.
16. R. B. SPACHT, W. S. HOLLINGSHEAD, and J. G. LICHTY. Wing-Stay 100 as an Antioxidant and as an Antiozonant.
17. J. C. PATRICK. Charles Goodyear Medal Lecture, Comments on Polysulfide Elastomers.

#### GENERAL PAPERS: HIGH TEMPERATURE RESISTANCE

S. C. NICOL, *Presiding*

18. R. M. KELL, B. BENNETT, and P. B. STICKNEY. Transition Behavior of Polychloroprene and Polychloroprene/SBR Blends.
19. A. D. DINGLE, and N. S. GRACE. The Dynamic Properties of Elastomers Measured Continuously with Temperature.
20. F. M. SMITH, and W. A. SMITH. Effect of Compounding or Processing Variations on the High Temperature Properties of Hevea and Butyl Rubbers.
21. R. E. CLAYTON. Heat Resistance of a Chlorine Containing Copolymer Isolefin and Multiolefins.
22. R. A. HAYES. The High Temperature Properties of Elastomers Containing Carboxyl Groups.
23. G. A. GALLAGHER, T. D. EUBANK, and A. L. MORAN. Compounding 'Viton' Fluoroelastomer for High Pressure, High Temperature Applications.
24. A. L. MORAN, R. P. KANE, and J. F. SMITH. Safe Processing Curing Systems for 'Viton' Fluoroelastomers.
25. K. C. BEACH, V. E. LOWERY, and L. F. COMPER. Banbury Processing Characteristics of SBR and NBR Rubbers.

## GENERAL PAPERS: NEW ELASTOMERS AND ADHESIVES

A. E. LAURENCE, *Presiding*

26. FRANKLIN S. C. CHANG. A Comparison of Tack Testing Methods for Pressure-Sensitive Tape.
27. A. L. MILLER, and S. B. ROBISON. Studies in Tire Cord Adhesion.
28. W. L. THOMPSON, T. B. MARSHALL, and A. T. SWEET. An Aqueous Blocked-Isocyanate 'Dacron' to Rubber Adhesive, Part I.
29. L. W. PARKE. An Aqueous Blocked-Isocyanate 'Dacron' to Rubber Adhesive, Part II.
30. T. C. WILLIAMS, R. A. PIKE, and F. FEKETE. Cyano Silicone Elastomers, A New Class of Solvent Resistant Rubbers.
31. R. S. STEARNS, and L. E. FORMAN. The Stereospecific Polymerization of Isoprene with Lithium and Organolithium Compounds.
32. H. E. RAILSBACK, W. T. COOPER, and N. A. STUMPE. *cis*-Polybutadiene-Natural Rubber Blends.
33. LAWRENCE SPENADEL, and ROBERT J. GOOD. The Development of a Synthetic Rubber for Self-Sealing Fuel Tanks for Aircraft.

## NEW BOOKS AND OTHER PUBLICATIONS

INTERNATIONAL SYNTHETIC RUBBER SYMPOSIUM. Published by Rubber and Plastics Age, Gaywood House, Great Peter Street, London, S.W.1, England. Paper bound,  $8\frac{1}{2} \times 11$  inches. Price \$4.20.—The bound edition of the complete papers given at the Symposium on Synthetic Rubber in March, 1957, is now available. The papers comprise: German Synthetic Rubber Developments, by Paul Baumann; Ameripol SN Rubber, by Robert P. Kenney; British Developments in Synthetic Rubber, by E. A. Murphy; Italian Synthetic Rubber Developments, by G. Natta; Nitrile and Other Acrylic Rubbers, by S. Mottram and P. H. Starmer; Self-Reinforcing Elastomers, by E. E. Gale; Effect of Cis-Trans Ratio on the Physical Properties of 1,4-Polybutadiene, by Gerard Kraus; Further Developments in the Field of Vulkollan, by Erwin Müller; Silicone Rubber, by P. C. Servais and I. H. Riley; Organic Fluorine Rubbers, by J. C. Tatlow; Neoprene Latexes, by E. P. Hartsfield; Relationship of Polymer Structure to the Properties of Butyl Rubber Vulcanizates, by W. L. Dunkel; Status of Butyl Tires in the United States, by D. J. Buckley; Butadiene-Vinyl Pyridene Copolymers, by W. Gumlich; A New Family of Elastomers, by R. M. Pierson; and Auxiliary Materials for Synthetic Rubber, by W. McG. Morgan. [Reviewed in *Rubber and Plastics Age*.]

POLYURETHANES. by Bernard A. Dombrow. Published by Reinhold Publishing Corporation, 430 Park Avenue, New York 22, New York. Hard cover,  $5\frac{1}{4} \times 7\frac{1}{2}$  inches, 176 pages. Price \$4.50.—One of the most remarkable developments since World War II in the application of new discoveries in the field of polymer chemistry has been the rapid rise in the production of polyurethanes, an estimated production capacity of 70 million pounds having been attained in the United States in 1957. In addition to films and fibers, these polymers are applicable as rubbers and as cellular elastomers, and as flexible foams they may prove a serious competitor to latex foam in cushioning applications. The development of these materials has been reflected in a vast amount

of published literature, and a survey of the whole field is thus particularly welcome at the present time. The book under review is designed to interest non-technical staff as well as to help the chemist to revise his knowledge of polyurethanes, and contains an introduction to the chemistry of these polymers and reviews their applications as rigid foams, semi-rigid foams, flexible foams, rubbers, adhesives, coatings, and in association with textiles. Apart from a brief acknowledgment of German work in this field in the period 1937-1945, the book is mainly concerned with American developments since 1945, but with that proviso in mind it comprises a useful introduction to the properties to be expected from materials based on polyurethanes. The discussion of polyurethane rubbers, which are characterized by high abrasion resistance, high tear strength, and excellent shock absorption, includes notes on Vulcollan, Chemigum SL, Vulcaprene A, and Adiprene, and mentions a new elastomer currently in the development stage, Adiprene L, which may be cured by polyols, titanate esters, and amines. In reviewing flexible foams the patented method and apparatus of the Mobay Chemical Company for mixing and dispensing the polymer is particularly described, and the properties of the product and some of the formulation variables affecting them are indicated. A brief commentary on the handling precautions associated with diisocyanates, and a short bibliography complete this handbook, which is attractively produced and adequately, though tersely, indexed. [Reviewed in *Rubber Journal and International Plastics.*]

ENCYCLOPEDIE TECHNOLOGIQUE DE L'INDUSTRIE DU CAOUTCHOUC. Vol. I. PRODUCTION DU CAOUTCHOUC NATUREL. FABRICATION DES CAOUTCHOUCS ARTIFICIELS. Edited by G. Genin and B. Morisson. Published by Dunod, 91 Rue Bonaparte, Paris 6<sup>e</sup>, France. Cloth cover, 6 × 9 inches, 666 pages, 124 illustrations. Price \$18.28.—The first section of the book, dealing with the various aspects of the production of natural rubber, is comprised of 11 chapters covering 292 pages. The first chapter, by R. Fabre, contains a masterly review of the economic aspects surrounding the production of natural rubber. The account of "Special Rubbers," in Chapter 5, by G. Giger, is complete, practical and sober in that it does not attempt to make light of the commercial difficulties involved. The same is true of Chapter 4, "Properties and Preparation of Natural Rubber," by P. Compagnon, M. Liponski, and J. D'Auzac. A particular disappointment is Chapter 7 on the "Preservation and Concentration of Latex," by H. P. Stevens and W. J. S. Naunton. These are great names, but the chapter is one of the weakest in the book. Fortunately, many of its omissions are included in the account by Madame J. Gleizes in Chapter 11 on the "Natural Latexes of Commerce." Unfortunately, the table of types of latex which she gives includes a considerable number of types which disappeared from the commercial market nearly 20 years ago. However, most of the other authors obviously are in close touch with the subjects on which they write. M. Favier, for example, contributes Chapter 9 on the "Stocking and Transport of Latex in the Consuming Countries," a subject in which he has had many years' experience both in England and in France. The length of chapter in the first section has been regulated to correspond with the commercial importance of the subject, but the account of "Wild Rubbers," by J. G. Bouychou (Chapter 3), and of "Gutta Percha and Balata" (Chapter 10), by H. R. Braak, although brief, is of the high standard which has been set throughout the book.

The second part of the book, 13 chapters covering 362 pages, has obviously presented greater difficulty than the first. The complicated series of operations

involved in the manufacture of a synthetic rubber can rarely fall within the personal knowledge and experience of any one author and even where this is the case, the author is probably precluded by commercial considerations from publishing too much of the 'know how' of his particular organization. It is no doubt such considerations that render Chapter 11 on the "Manufacture of Neoprene," by R. E. de Puy, and Chapter 12 on the "Industrial Manufacture of Butyl Rubber," by Maurice Moulin, not only short but lacking in information. In this second section of the book there are accounts of the manufacture of the chief monomers used for synthetic rubber. These include "Isoprene" (Chapter 6), by A. Valet, "Styrene" (Chapter 8), by Otto Dorrer, and "Acrylonitrile" (Chapter 9), by D. H. Holzrichter. There are three chapters on the manufacture of butadiene, one describing methods from petroleum (Chapter 3), by Michel Guinot, alcohol (Chapter 4), by R. Buret, and acetylene (Chapter 5), by Otto Dorrer. The longest chapter in this section is by J. B. Donnet, concerning elastomers of the Buna type. The time which has elapsed between the submission of manuscripts and the publication of the book may explain the absence of any account of the newer rubbers. Despite these criticisms, the book is to be strongly recommended. (Volume II of the Encyclopedie is in preparation. Volumes III and IV have already been published and were reviewed in *RUBBER CHEM. & TECHNOL.*, Vol. 29, No. 3 (1956).) [Edited from the review by H. J. Stern which appeared in *Rubber Journal and International Plastics*.]

**MACHINERY AND EQUIPMENT FOR RUBBER AND PLASTICS. Vol. II. SUPPLEMENTARY MACHINERY AND EQUIPMENT.** Compiled by R. G. Seaman. Published by Rubber World, 386 Fourth Avenue, New York 16, New York. Cloth cover, 6 × 9 inches, 714 pages, 300 illustrations. Price \$15.00 (U.S.A.), \$16.00 (elsewhere).—The first volume of this two-volume work was issued in 1952 and covered the primary machinery and equipment used in the rubber and plastics industries, such as mills, mixers, calenders, extruders, presses and molds, as well as specific equipment for such specific needs as tires, hose and belting, footwear, wire and cable, soles and heels, and latex products. In view of the complete absence of a comprehensive text book on the manufacture of rubber products it filled a long felt need. This second volume, devoted to supplementary machinery and equipment, the first of its kind, fills another important gap.

The format of this second volume follows that of the first, namely, for each classification there are furnished data on types, specifications, design features, operation and applications, as well as names and addresses of the manufacturers or suppliers. Adding to the value of the book are the introductory articles which precede each chapter, each prepared by a recognized authority in the respective fields. In one chapter, that covering handling and storage, there are three such introductory articles, devoted to waterproof footwear, mechanical goods and the plastics industry, respectively.

In all, the book covers eleven classifications, as follows: (1) Weighing and Measuring; (2) Handling and Storage; (3) Valves and Piping; (4) Pumps; (5) Air Handling Equipment; (6) Size Reduction and Separation; (7) Fabricating and Finishing; (8) Decorating and Assembly; (9) Power Transmission; (10) Lubrication; (11) Steam Generation. Many of these classifications are subdivided into five or more elements. For example, the section on "Fabricating and Finishing" is divided into cutters (of all kinds), machining accessories,

vacuum forming equipment, finishing equipment and accessories. As indicated above, it is comprehensive in its scope and is a welcome addition to the literature. [Reviewed in *Rubber Age* (N. Y.).]

**THE IMPACT TEST IN MATERIAL TESTING.** By Wilhelm Späth. Published by A. W. Gentner Verlag, 131 Fortstrasse, Stuttgart, West Germany. Hard cover,  $6 \times 8\frac{1}{2}$  inches, 180 pages, 64 figures. Price \$5.25.—(In German.) This is an informative, comprehensive account of impact testing methods and results for a great variety of materials, e.g., steel, plastics, elastomers, sintered materials, concrete, glass, etc. The first section lists specifications, test equipment, results, and theories making use of the latest literature. The second section describes a new impact tester which enables the peak impact load to be measured mechanically, as well as the impact energy. The author's wide ranging investigations with this equipment are recounted. The third section discusses the role of impact tests in material testing, the wide variety of phenomena encountered, and the usefulness of the methods for dealing with problems of tough and brittle breaks. The concepts of toughness and brittleness are examined and the elementary physical phenomena taking place at break are analyzed.

The book contains a wealth of suggestions and new aspects for impact testing with helpful discussions of sources of error and ways of eliminating them. The book should be helpful for everyone working with or using the results of impact tests. [Reviewed for **RUBBER CHEMISTRY AND TECHNOLOGY** by S. D. Gehman.]

**RUBBER AND PLASTICS.** By Wilhelm Späth. Published by A. W. Gentner Verlag, 131 Fortstrasse, Stuttgart, West Germany. Hard cover,  $6 \times 8\frac{1}{2}$  inches, 280 pages, 101 figures. Price \$6.56.—(In German.) This book gives a unique presentation of basic concepts of the mechanical characteristics of polymers in relation to testing evaluations and properties of technical importance. The emphasis is entirely on the physical rather than on the chemical structure of the materials. There are three main sections. The first deals with such subjects as internal and external friction and their relationship to ultrasonic vibrations and heat generation; model concepts of polymer structure and their limitations; microscopic and submicroscopic failure processes; phenomenological realization of elementary processes such as relaxation, creep, and flow. The second section is concerned with technical testing procedures for evaluating the effects of mechanical loading and contains descriptions and analyses for a wide variety of procedures for tensile testing, hardness testing, dynamic tests, etc. The subject of residual stresses is given especial attention. The third section contains examples of practical testing procedures chosen to illustrate their connections with the general concepts of mechanical behavior developed in the first two sections. Here are discussed subjects such as the shape of diverse stress-strain curves; effects of temperature on stress-strain curves and other properties, cold stretching; fatigue testing; etc.

The general treatment of the material in the book is new and distinctive. It contains information which will be widely useful for many technological aspects of rubber and plastics. [Reviewed for **RUBBER CHEMISTRY AND TECHNOLOGY** by S. D. Gehman.]

**THE ANALYSIS OF RUBBER AND RUBBER-LIKE POLYMERS.** By William C. Wake. Published by Maclaren & Sons, Maclaren House, 131 Great Suffolk Street, London, S.E.1, England. Cloth cover,  $5\frac{1}{2} \times 8\frac{1}{2}$  inches, 238 pages. Price \$8.00. (This book is available from the Book Department, *Rubber Age*, 101 West 31st Street, New York 1, New York.)—It is a pleasure to be able to refer to the introduction of a serious work as being enjoyable, free and readable in style, with a hint of dry humor expertly used. This section presents a logical clear view of the polymers considered, the analytical problem, the scope of the book and the general principles involved. It is informative to the uninitiated without offending the experienced.

The book continues in this vein through eleven comprehensive chapters of useful information and critical discussion, much of which will be new to rubber analysts in this country. The fault with the choice of content, if any, lies in the absence of detail on British Standards Institution methods, which are not generally available here.

There is an excellent chapter on extraction theory and practice containing much common sense information on interpretation and many useful suggestions for American analysts concerning extraction solvents and methods. The chapter on qualitative analysis for polymer type is to be recommended for its completeness and its logical chemical and spectroscopic approach to the subject. Some relatively unknown methods of attack are discussed here. Dr. Wake questions the reasons for survival of some standard American methods. He could not know that a critical review of these methods is in progress and that some of the methods have been found to be in effective use while others will be revised or eliminated.

In the chapter on elemental analysis we find a strange mixture of methods we normally consider to be obsolescent or too slow for practical use with some very modern analytical methods of great value. The reader should be able to study this chapter in the light of his own experience and profit by it. The discussion of unsaturation methods in the chapter on polymer functional group analysis is of particular value, especially when linked with the excellent and unusual chapter on solution and dissolution methods of treating polymers prior to analysis. There is fertile field here although we reserve the right to question the validity, or perhaps the interpretation, of unsaturation values determined on a dissolved polymer which has been strongly aerated at  $180^{\circ}\text{C}$ .

The entire subject of analysis of extracts for sulfur, accelerators, antioxidants or plasticizers is very adequately treated, the modern chromatographic methods being clearly described. The author is rightly concerned here with some standard American methods and definitions involving free sulfur. There is also a brief and lucid exposition in the final chapter on the value and fundamental uses of statistical methods in studying the causes of variance in rubber analysis.

We feel strongly that this book is essential to proper operation of a modern rubber analysis laboratory, large or small. [Reviewed by Willard P. Tyler for *Rubber World*.]

**Research Memorandum: Skim Rubber.** Due to the steadily growing production of concentrated latex on the plantations, skim rubber, made by coagulating the byproduct "skim" latex, is coming on to the market in increasing quantities. Of necessity from its mode of production, it has an unusually high content of nonrubber substances such as proteins, and hence is liable to behave abnormally and give trouble in manufacturing processes.

As a result of discussions initiated by the tire manufacturers, the Research Association of British Rubber Manufacturers made a study of the properties of skim rubber and the best ways of using it. These investigations included samples made by special processes designed to reduce the nonrubber content.

This work showed in particular that correct choice of accelerator does much to reduce the scorching tendencies of skim rubber, and that the special processes used in preparing certain of the samples give them much more nearly normal scorch and cure characteristics. It was further found that blending with GR-S provides a useful alternative method of using skim rubber; such skim-GR-S blends gave good results in resin-rubber shoe soling compounds, for instance.

This and other useful information concerning skim rubber is set out in full in a report (Research Memorandum R410) issued by the Research Association of British Rubber Manufacturers. A limited number of copies of this report are available at a cost of 5/- each, and can be obtained on application to the Secretary, RABRM, Shawbury, Shrewsbury, Shropshire, England.

Report of the Chairman of the Bibliography Committee to the Executive Committee of the Division of Rubber Chemistry. August 22, 1958. I am very pleased to state that the editorial work of the Bibliography Committee is in better shape as of today than it has been at any time of its existence. We are practically up to date. All the references through 1956 have been assembled, edited and are ready for the editor-in-chief; all the references for 1957 have been assembled on cards and are now being edited; work has begun on the collecting of the 1958 references.

Our schedule is as follows:

1952-54 Edition to be printed	October 1958
1955-56 Edition to be printed	April 1959
1957-58 Edition to be printed	March 1960

Furthermore you can see from the table below that the number of references is increasing very fast. This means *increased costs*. For this reason I am going to ask you to expect higher budgets for the coming editions. We are trying to make complete coverage and also maintain all of the good features of the Bibliography. It will be seen also from the table that the number of references per year will be in the 1957-58 edition three times the number it was in the 1940-41 edition.

Edition date	No. ref. per edition	No. ref. per year	Cost per edition	No. members of comm.
1940-41	3350*	1675	3378	5
1942-43	3850*	1925	7738	7
1944-45	4903*	2451	10554	7
1946-48	5950*	1983	11605	9
1949-51	6412*	2137	12600	10
1952-54	9001*	3000	?	12
1955-56	7010*	3505	?	13
1957-58	9100**	4550	?	15

\* Actual.

\*\* Estimated (1957).

Respectfully submitted,

JOHN McGAVACK  
Chairman Bibliography Committee

## FIFTIETH ANNIVERSARY OF THE TEACHING OF RUBBER CHEMISTRY AT AKRON UNIVERSITY

Rubber scientists, researchers and educators interested in the research, physical and chemical development aspects of the rubber industry met on the campus of the University of Akron on Friday, October 3, 1958, to join faculty, students and alumni in celebrating the Fiftieth Anniversary of the Teaching of Rubber Chemistry at the University and to participate in ceremonies establishing the Rubber Science Hall of Fame on the Akron campus.

Dr. Norman P. Auburn, President of the University, opened the all-day program at a morning convocation. Honorary degrees of Doctor of Science were awarded to Dr. Alan T. Waterman and Dr. G. Stafford Whitby.

Following an informal luncheon, Dr. Maurice Morton, Director of the Institute of Rubber Research and Professor of Polymer Chemistry, led an afternoon symposium on "Macromolecules and Elastic Networks". Participating in the symposium were George Stafford Whitby, Consultant on Rubber Research and Professor Emeritus of Rubber Chemistry at the University of Akron; Peter Debye, Nobel Award winner in 1936 and Professor Emeritus of Chemistry at Cornell University; and P. J. Flory, Executive Director of Research, Mellon Institute. Dr. Whitby's topic was "A Fifty-Year Retrospect of Rubber Science"; "Measurements of Macromolecules" was Dr. Debye's topic; and Dr. Flory discussed "Rubber Elasticity".

Establishment of the Rubber Science Hall of Fame followed the symposium. The naming of the first members, chosen by a committee of scientists from the Division of Rubber Chemistry, American Chemical Society, and the faculty of the University, prior to the October 3 program, was a high point of the afternoon program. Portraits of Hall of Fame members hang in the chemistry library, temporarily located in Knight Chemical Laboratory, the home of chemistry activities at the University. It is expected that one person will be added each year to the Rubber Science Hall of Fame.

Members of the committee appointed for the observance included: Harry P. Schrank, Executive Vice-President of Seiberling Rubber Company and Vice-Chairman of the Board of Directors, University of Akron, chairman; Dr. Auburn; Lawrence M. Baker, Factory Manager, General Tire and Rubber Company; George W. Ball, Director of University Relations, University of Akron; E. H. Cherrington, Jr., Dean, Buchtel College of Liberal Arts, University of Akron; Otis D. Cole, Assistant Director of Chemical Laboratories, Firestone Tire and Rubber Company; James D. D'Ianni, Assistant to Vice-President for Research, Goodyear Tire and Rubber Company; Dr. Morton; Waldo Semon, Director of Polymer Research, B. F. Goodrich Company; and Dr. Thomas Sumner, Head of the Department of Chemistry at the University. An evening banquet featured an address by Dr. Alan T. Waterman, Director, National Science Foundation. Dr. Waterman's subject was "Basic Research and Industrial Progress".



# RHEOLOGICAL MEASUREMENTS FOR THE CHARACTERIZATION OF HIGH POLYMERS \*

KURT EDELMANN AND EDITH HORN

DEUTSCHE AKADEMIE DER WISSENSCHAFTEN ZU BERLIN INSTITUT FÜR  
FASERSTOFF-FORSCHUNG TELTOW-SEEROFF, BERLIN, GERMANY

## INTRODUCTION

During the last decade, rheology—the science of flow—has steadily grown in stature. Since it is a relatively new branch of learning, its boundaries are not sharply defined. Rheology treats primarily the problems of deformation and flow of easily deformed substances, that is, the flow of fluids, the anomaly of viscosity and plasticity of colloidal molecules, as well as the phenomena of relaxation and the thixotropy of dispersed systems.

Today, rheological problems are found in nearly every industrial field. Hence it is impossible to list all the results of rheological studies which find application in industrial production processes as well as in research work and plant design. Thus Meskat<sup>1</sup> has shown the viscosity variation of two cellulose solutions in the shearing stress regions of various industrial devices. Specifically as rheologically important, the following substances should be listed here: all high polymers, glues, resins, natural and synthetic fibers, rubber cements, gelatin, starch, proteins, fats and other products of the food industries, dyes, greases, oil and bitumens, drilling muds, slag and silicate melts. The construction and operation of machines to transport and process the above materials demand a knowledge of their rheological properties. If one now considers, for example, a high polymer solution possessing a dynamic viscosity of 1000 poises at minimum shear stress and which decreases to 0.01 poise at high shearing stress then the importance of understanding rheological behavior becomes evident. In a similar manner, the viscosity of greases can vary by 10<sup>8</sup> according to the shearing stress. Determining the flow behavior of various systems by a single measurement is no longer sufficient, but obtaining the flow curve is requisite as Philippoff<sup>2</sup> has first shown. In preparing such a flow curve measurements are necessary that cover a range of 10<sup>4</sup> to 10<sup>6</sup> in both shearing stress and velocity gradient. Since the capillary method offers the most accurate procedure for viscometry, the following will give, from the author's experiments, the details of performing rheological measurements with the Umstätter structural viscometer based on the capillary principle.

## THEORY

According to Newton, the viscosity  $\eta$  in poises is defined as the proportionality factor between the shearing stress  $P$  in dynes/cm<sup>2</sup> and the velocity gradient  $G$  in  $s^{-1}$

$$\eta = \frac{P}{G} \quad (1)$$

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Plaste und Kautschuk*, Vol. 4, pages 84 to 87 (1957).

This viscosity relationship applies to laminar flow in capillaries and leads to the Hagen-Poiseuille law

$$\eta = \frac{\pi r^4 p}{8QL} \text{ poises} \quad (2)$$

Here  $r$  signifies the capillary radius in cm,  $L$  the capillary length in cm,  $p$  the applied pressure in atmospheres converted to dynes/cm<sup>2</sup> through multiplication by 981,000, and  $Q$  the efflux volume in cm<sup>3</sup>.

Equilibrium prevails in the capillary stream when the force  $K$ , which the pressure  $p$  develops on the face of the capillary, is equal to a tangential force that is the shearing stress  $P$ , which is exerted on the surface of the unit.

For this equilibrium

$$K = \pi r^2 p = 2\pi r L \cdot P \text{ dynes} \quad (3)$$

from which may be obtained the relation for the shearing stress  $P$

$$P = \frac{rp}{2L} \text{ dynes/cm}^2 \quad (4)$$

Likewise the following equation defines the velocity gradient  $G$ ,

$$G = \frac{4Q}{\pi r^2 t} \text{ s}^{-1} \quad (5)$$

wherein  $t$  represents the flow time in seconds. This velocity gradient is measured on the edge. The mean velocity gradient  $\bar{G}$  according to Kroepelin<sup>3</sup> is

$$\bar{G} = \frac{2}{3} G \quad (6)$$

Because of the simple relationships in these accurately determined quantities, capillary viscometry assumes the greatest importance.

Pure liquids like water, hydrocarbons, and solutions of low molecular weight materials follow Newton's viscosity definition. In spite of variations in the magnitudes  $r$ ,  $L$ , and  $p$ , the same value for  $\eta$  is obtained. However, even slight amounts of macromolecular substances, especially those having linear molecules, increase the viscosity of their solvents so greatly that deviations from Newtonian behavior occur. These non-Newtonian liquids show a viscosity dependent on the shear stress. Their flow behavior is defined by the functional dependency between shear stress  $P$  and velocity gradient  $G$ . It is

$$G = f(P) \quad (7)$$

The viscosity of such liquids is therefore no longer a specific constant, or a proportionality factor between shear stress and velocity gradient, but a function of both. Therewith a single viscosity measurement gives only an apparent viscosity  $\eta'$  which is dependent on the experimental conditions.

This viscosity  $\eta'$  can decrease with increasing shear stress, but above all it can increase at higher concentrations or not even reach a stationary condition<sup>4</sup>. The decrease of the viscosity with shear stress was denoted as structural viscosity by Wo. Ostwald, whereby the hypothesis was established that a structural variation appears in the liquid through the flow process. On the other hand, the increase of viscosity with shear stress is called rheopexie, which is caused by

a solidification as a result of the flow process. Further, according to the history of the system to be examined, threshold values for both shear stress and velocity gradient may appear.

Above all, the appearance of structural viscosity is observed in the solutions of high polymers. The only commercial viscometer which permits the viscosity measurements necessary for the plotting of flow curves in a shear stress and rate of flow range over  $10^4$ , is the structural viscometer of Umstätter. Since this viscometer operates on the capillary principle, it yields the most accurate results with a reproducibility of  $\pm 1\%$ , when the greatest range is considered. In order that characterization of high polymers by their flow curves in different solvents may reach wider use, the details of the ideal procedure for rheological measurement with this structural viscometer will be described and the resulting calculations will be explained.

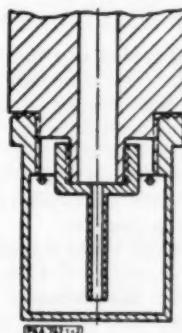


FIG. 1.—Cylindrical container with threaded holes near top edge and attached riser.

#### EXPERIMENTAL PROCEDURE

The Umstätter structural viscometer consists essentially of a thick-walled steel bomb and removable cover in which the measuring capillary is inserted. Since the structural viscosity of solutions of high polymers is influenced by the duration in the capillary, a 10 cm capillary works best. It is recommended that a set of capillaries with diameters of 2.0, 1.5, 1.0, 0.6, 0.4, and 0.2 mm be cemented with litharge-glycerine cement into metal cases of brass or V4A-material. The largest capillary is used first, followed by the smaller ones in decreasing order.

The most suitable container for the solutions to be measured is a cylindrical device of V4A with threaded holes near the upper edge through which gas, compressed air or nitrogen, exerts pressure on the surface of the solution as in a syphon (Figure 1). A riser must be inserted in the rim nut to fasten the capillary in the cover which reaches to the bottom of the container. With especially viscous solutions in the range of high shear stresses one may find the impressed gas channeling through the solution and gas bubbles issuing from the capillary. It is best then to use a container with an adjustable bottom (Figure 2) which prevents the contact of the impressed gas with the experimental solution. In this case, the measuring capillary need be held only by a rim nut screw in the cover.

For insertion of the measuring capillary the cover is placed on the head of

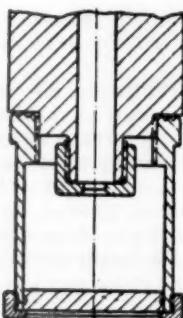


FIG. 2.—Container with adjustable bottom and rim nut.

the viscometer, a gasket of hard rubber or a fibrous material put in, and some experimental solution poured in. The front part of the capillary is dipped into the experimental solution and then slipped in the cover, until it strikes the packing disc. Some experimental solution is now added to the end of the capillary and the rim nut with a rising tube attached. In this way, the capillary is covered completely by the liquid packed in the cover. An extreme tightening of the rim nut is not necessary since the capillary is pressed ever more tightly against the gasket with increasing pressure.

Now the container is filled nearly to the threaded holes with the experimental solution previously filtered through a G-1-frit and the cover attached. A strong tightening of the threads is not necessary. With this arrangement the cover is placed in the steel bomb and securely tightened with a wrench. In spite of everything some leakage of compressed gas at high pressures has no effect on the accuracy of measurement.

The applied pressure, also called the transpiration pressure, is obtained from a gas cylinder by pressure from tubing leading through a pressure regulating valve to the viscometer. The coarse adjustment for each required pressure is secured by the regulator at the cylinder and only the fine adjustment at the low pressure gage is secured with the needle valve of the structural viscometer. It is advisable to tap the gage at short time intervals to overcome the resistance (or lag or inertia) of the indicator. Three fine measuring gages are used for the measurements, 0 to 1 atm, 0 to 10 atm and 0 to 100 atm. Measurements begin with the lowest pressure.

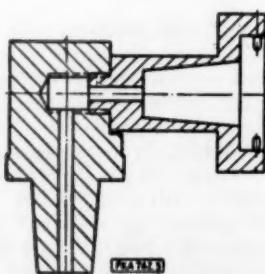


FIG. 3.—Elbow connection with bayonet seal and conical gasket for the horizontal microburst.

Since the large amount of metal in the apparatus requires nearly an hour to reach a constant temperature, the circulating thermostat connected to the heating mantle is started to initiate the experiment. When this constant temperature is reached, measurements can be started. Now the largest capillary is inserted and the 0 to 1 atm gage is attached.

With the needle valve open, the regulator on the cylinder is opened slightly until gas escapes. Then the needle valve on the viscometer is partially closed until a slight pressure registers on the gage. This pressure forces the experimental solution through the capillary. After a short time, first some bubbles issue from the cover and finally the bubble-free solution appears. However if the stream of bubbles does not stop or even increases, the capillary is not tightly inserted. The viscometer must be dismantled again and the capillary, sealed with more liquid, reinserted. The beginning of the flow depends on the viscosity of the solution, which in turn depends on concentration and molecular weight. If the solution flows too fast at the lowest pressure, the capillary is exchanged for a narrower one.

As soon as the solution issues slowly and bubble-free from the cover, the microburet with bayonet seal and conical gasket is set up to collect and measure the solution forced through the capillary. To avoid hydrostatic pressure corrections the microburet is used horizontally up to pressures of about 10 atm. An elbow (Figure 3) fitted with the same bayonet seal and conical gasket has proved useful at this point. Only at higher pressures is the microburet directly attached vertically.

To be able to make successive measurements at different pressures as fast as possible, three persons work best together. One person regulates and keeps the pressure constant, the second reads off the graduation of the microburet for a fixed volume and with a stop watch, simultaneously measures the time required for this volume; and the third records the values of pressure, volume, and time.

With this measuring method the entire flow curve can be surveyed within two hours over a  $10^4$  range of the velocity gradient. Two fillings of the container suffice.

Additionally, a point of the flow curve in the lower range of the velocity gradient can be ascertained with certainty with the free flow which lies in the range of  $\eta_0$ , the viscosity at rest. Here  $\eta$  can be determined directly with  $K$ , the known calibration constant of the apparatus, according to the equation

$$\eta = K \cdot t \cdot p \text{ (centipoise)} \quad (8)$$

and  $G$  according to Equation (5), while  $P$  can be calculated by Equation (1).

#### MATHEMATICAL EVALUATION

The mathematical procedure for calculating the points for the flow curve are shown for example, with a 2% solution of natural rubber in toluene.

##### FREE FLOW UMSTÄTTER VISCOMETER WITH A CAPILLARY DIAMETER OF 0.41 CM

Volume of all three bulbs	$Q = 9.15 \text{ cm}^3$
Apparatus constant	$K = 0.1903$
Efflux time	$t = 1302 \text{ seconds}$
Sp. gr. of solution	$= 0.864$
From which results	$R^* = 3.504 \cdot 10^{-4}$
	$= 214 \text{ cP} = 2.14 \text{ poises}$
	$G = 2.45 \cdot 10^4$
	$P = 5.24 \cdot 10^4$

*Umstätter's structural viscometer.*—From the data appearing in Table I,  $P$  is calculated by Equation (4) and  $G$  by Equation (5), while the apparent viscosity  $\eta'$  is ascertained either directly by Equation (2) or from  $P$  and  $G$  by Equation (1).

If, corresponding to the proposal of Philippoff<sup>6</sup>, the values for  $G$  and  $P$  are plotted on double logarithmic coordinates, the flow curve is obtained. Since in Newtonian liquids the velocity gradient increases proportionally to the shear stress, a straight line plot of exactly 45° is obtained (Figure 4). On the other

TABLE I  
DATA FOR THE FORMULATION OF THE FLOW CURVE OF A  
2% RUBBER SOLUTION IN TOLUENE

Experimental conditions			Experimental data				Calculated		
Capillary dia., cm.	Manometer at	At.	Volume from-to	S	cm <sup>3</sup>	P	G	$\eta'$	
						dyn/cm <sup>3</sup>	s <sup>-1</sup>	poise	
0.06	0-1.0	0.10	0.08-0.1	11.18	0.02	1.47·10 <sup>3</sup>	8.45·10 <sup>1</sup>	1.74	
		0.14	0.2-0.25	16.68	0.05	2.06·10 <sup>3</sup>	1.42·10 <sup>2</sup>	1.45	
		0.20	0.5-0.55	9.05	0.05	2.95·10 <sup>3</sup>	2.61·10 <sup>2</sup>	1.13	
		0.60	2.1-2.3	5.57	0.2	8.83·10 <sup>3</sup>	1.69·10 <sup>2</sup>	0.523	
	0-10	0.80	3.1-3.6	8.37	0.5	1.18·10 <sup>4</sup>	2.82·10 <sup>3</sup>	0.419	
		1.2	0.1-0.2	5.34	0.1	1.18·10 <sup>4</sup>	2.99·10 <sup>3</sup>	0.395	
		1.4	0.4-0.6	8.00	0.2	1.37·10 <sup>4</sup>	3.98·10 <sup>3</sup>	0.344	
		1.6	0.9-1.1	6.62	0.2	1.57·10 <sup>4</sup>	4.81·10 <sup>3</sup>	0.326	
0.04	0-100	6.0	0.15-0.25	7.04	0.1	2.95·10 <sup>4</sup>	1.81·10 <sup>4</sup>	0.163	
		8.0	0.5-0.7	9.14	0.2	3.93·10 <sup>4</sup>	2.79·10 <sup>4</sup>	0.141	
		10.0	1.0-1.3	10.14	0.3	4.91·10 <sup>4</sup>	3.77·10 <sup>4</sup>	0.130	
		15.0	2.2-2.4	4.08	0.2	7.35·10 <sup>4</sup>	6.24·10 <sup>4</sup>	0.118	
		20.0	2.8-3.2	5.15	0.4	9.81·10 <sup>4</sup>	9.88·10 <sup>4</sup>	0.099	
		25.0	3.8-4.4	5.65	0.6	1.23·10 <sup>5</sup>	1.35·10 <sup>5</sup>	0.091	
		40.0	0.0-1.5	8.21	1.5	1.96·10 <sup>5</sup>	2.33·10 <sup>5</sup>	0.084	
		50.0	3.0-5.0	8.75	2.0	2.45·10 <sup>5</sup>	2.91·10 <sup>5</sup>	0.084	
		60.0	0.0-2.0	7.27	2.0	2.95·10 <sup>5</sup>	3.50·10 <sup>5</sup>	0.084	

hand, in the non-Newtonian fluids, the velocity gradient increases exponentially with the shear stress and the curves are steeper. This steepness runs through a maximum and a Gaussian error curve<sup>7</sup> is obtained for

$$\frac{d \ln G}{d \ln P} = \sigma \text{ (oiliness)}$$

Thus the symmetry of the flow curve also is explained. At low shear stresses, the solutions of high polymers show Newtonian flow behavior and this part of the flow curve is designated  $\eta_0$ , the viscosity at rest. Likewise at high shear stress, Newtonian flow reappears this being the range of  $\eta_\infty$ . Between these ranges lies the range of non-Newtonian flow, the range of structural viscosity, with a maximum slope in the middle. This maximum, the inflection point of the flow curve, is the critical point, and, as critical velocity gradient  $G$  it is a characteristic physical constant<sup>8</sup> dependent on the molecular weight of the dissolved high polymers.

The symmetry of the flow curve is today still sporadically doubted although no proof for such doubts has been advanced. Here too it can only be said that with the extensive experimental materials, which have been investigated for years both by Umstätter and also by the authors, not one single case of an unsymmetrical flow curve has been observed. In all systems which consist only

of solvent molecules and dissolved macromolecules, the flow curve shows a symmetrical course.

On the other hand in heterogeneous systems, suspensions, and emulsions, no symmetrical flow curve is to be expected.

If flow curves are plotted for solutions of high polymers with an average molecular weight under 100,000 it is still not possible to reach the range of  $\eta_{\infty}$  with materials available today. Here the symmetry of the flow curve offers an excellent possibility to estimate  $\eta_{\infty}$  since the distance between  $\eta_0$  and the inflection point is merely doubled. On the other hand, it can appear that in high polymers of very high molecular weights, in the range of the inflection point the

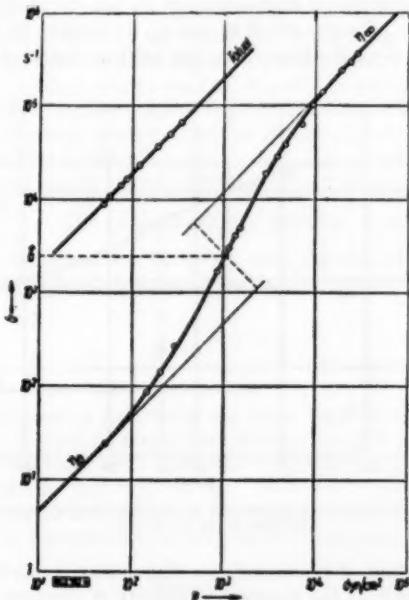


FIG. 4.—Flow curve of a 2% solution of natural rubber in toluene drawn by Phillipoff.

flow curve proceeds almost in a straight line over  $10^2$ , and the detection of the exact inflection point is difficult. In this case, the halving of the difference between  $\eta_0$  and  $\eta_{\infty}$  offers the possibility of detecting the inflection point. However, determining the inflection point most accurately from the straight flow curve is described later.

Ever since Umstätter<sup>10</sup> set forth a way to show structural viscosity as a function of the velocity gradient in the form of a straight line, other flow curve presentations have been introduced in which the apparent viscosity  $\eta'$ , according to Equation (2) is compared to the respective velocity gradient  $G$ , according to Equation (5), in a double logarithmic coordinate system.

Here too the exact knowledge of the capillary radius is necessary, which radius one can easily calculate for a standard from the Hagen-Poiseuille law

(Equation (2)) according to the equation

$$R = \sqrt{\frac{8 \cdot Q \cdot}{p \cdot t \cdot}}$$

where  $p$  signifies the gage pressure in atmospheres which is converted into dynes/cm<sup>2</sup> on multiplication by 981,000. Measurement of a standard oil in the viscometer provides data for this calculation.

Using the data from Table I, the flow curve of the cited 2% rubber solution is represented in this method of flow curve presentation in Figure 5. While here the Newtonian liquids, for example toluene, give a straight line parallel to the abscissa, the solutions of high polymers as non-Newtonian liquids show a symmetrical curve. The ranges of  $\eta_0$  and  $\eta_\infty$  lie parallel to the abscissa while the inflection point  $G$  of the flow curve lies halfway between these parallels.

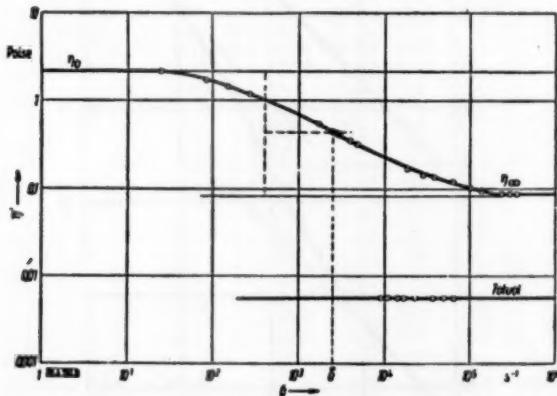


FIG. 5.—Flow curve of a 2% solution of natural rubber in toluene, plotted according to the new method.

This newer method of representing a flow curve is obvious since it shows directly by what amount the measured viscosity  $n'$  changes in the range from  $\eta_0$  to  $\eta_\infty$ , in the present case for some  $10^{1.5}$ . Hereby it is mentioned that changes above  $10^8$  were measured by the author in solutions of very inhomogeneous and very high molecular weight substances.

As already mentioned, the flow curve can also be prepared as a straight line<sup>10</sup>. On probability graph paper No. 297-1/2A<sub>4</sub> of Schleicher and Schull or No. 485 of Schafer's publishing house, Feinpapier, Plauen i. Vogtl., the abscissa is scaled logarithmically and the ordinate is scaled according to Gaussian integral. If the values for

$$\frac{\ln \eta/\eta_\infty}{\ln \eta_0/\eta_\infty}$$

are now plotted on the ordinate against the velocity gradient  $G$  on the abscissa, a straight line flow curve is obtained (Figure 6). Then one chooses at random a point on the flow curve in the range of  $\eta_\infty$  as the numerical value for  $\eta_\infty$ , likewise

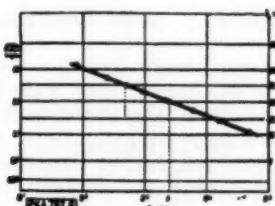


FIG. 6.—The straight line flow curve of the 2% solution of natural rubber in toluene, plotted by Umatäter.

a point for  $\eta_0$  and in addition a series according to a number of points in the range of non-Newtonian flow for the respective  $\eta$  with the  $G$  pertaining to it. If the flow curve preparation follows Figure 4,  $\eta$  must first be calculated according to Equation (1), while it can be read off directly in the preparation according to Figure 5. Here is a further advantage of this method of flow curve preparation. The mathematical procedure of the straight line for Figure 6 is given in the following (see also Table II).

In this probability graph paper, 100% on the ordinate corresponds to a value of 1 for  $\frac{\ln \eta / \eta_\infty}{\ln \eta_0 / \eta_\infty}$ . The critical velocity gradient  $\hat{G}$  can be read off very exactly at the intersection of the 50% line with the straight line flow curve. For calculating the absolute viscometric molecular weight<sup>11</sup> according to the equation

$$M = \frac{K \cdot c}{\hat{G}}$$

it is advisable in all cases to determine the value for  $G$  according to this procedure. To be sure, it must be stated here that in the cases in which  $\eta_\infty$  is non-ideal or not at all attainable with materials available today, a positive effort should be made to find the true value for  $\eta_\infty$ . However, it must be intentionally emphasized that the trial in this case is permissible since, from the previously drawn bases, the flow curves are symmetrical for all defined systems which in-

TABLE II

NUMERICAL VALUES FOR PLOTTING THE STRAIGHT LINE FLOW CURVE  
OF A 2% RUBBER SOLUTION IN TOLUENE

$G$	$\eta$	$\eta / \eta_\infty$	$\ln \eta / \eta_\infty$	$\frac{\ln \eta / \eta_\infty}{\ln \eta_0 / \eta_\infty}$
$8.0 \cdot 10^1$	1.70	20.2	3.0057	0.928
$2.4 \cdot 10^2$	1.23	14.6	2.6810	0.830
$5.0 \cdot 10^2$	0.91	10.8	2.3795	0.735
$9.0 \cdot 10^2$	0.70	8.31	2.1174	0.655
$2.2 \cdot 10^3$	0.46	5.46	1.6974	0.525
$6.0 \cdot 10^3$	0.28	3.32	1.1990	0.370
$1.6 \cdot 10^4$	0.18	2.14	0.7608	0.236
$4.9 \cdot 10^4$	0.123	1.46	0.3784	0.117

$$\eta_\infty = 0.0842$$

$$\ln \eta_\infty = 0.5254 - 3$$

$$\eta_0 = 2.14$$

$$\ln \eta_0 = 0.7608$$

$$\ln \eta_0 / \eta_\infty = 0.7608 - 0.5254 + 3 = 3.2354$$

clude solutions of high polymers. On the other hand, this is not allowed in heterogeneous systems.

Moreover, the slope of the straight line flow curve on probability paper brings about the concept of non-homogeneity in the high polymers concerned. The steeper the straight line proceeds, the more uniform are the high polymer molecular weights. A possibility for obtaining a numerical value for this inhomogeneity  $U$  arises from a proposal by Umstätter, that the projection, in cm, of the straight line curve between the 75% and 25% line on the abscissa be divided by abscissa units in cm and expressed in decibels. The procedure for determining inhomogeneity is illustrated in Figure 6 whereby the following values were obtained.

$$U = \frac{13.1}{9} \text{ cm} = 1.4556 = 14.55 \text{ dec}$$

As shown in the example with a 2% solution of natural rubber in toluene, it is easily possible with the steps described in this work to determine a complete flow curve above  $10^4$ - $10^6$  within two hours with the sole or only commercial structural viscometer by Umstätter. Likewise, there is no difficulty with the mathematical calculations needed to obtain simultaneously both a material constant dependent solely on the molecular weight and an absolute value for the inhomogeneity. Thus it can be expected that the practice of characterizing high polymers will increasingly refer to the flow behavior of high polymer solutions by their material constants.

#### CONCLUSION

Since the Umstätter structural viscometer represents the only viscometer that operates on the capillary principle, the most accurate measuring principle in viscometry, with a shear stress range above  $10^4$ , this paper describes the necessary steps, from the long term experience of the authors with this apparatus, which permit a rapid and true determination of a complete flow curve. Also the necessary calculations are given and explained in an example. From this method, the critical velocity gradient  $\dot{G}_c$ , the inflection point of the flow curve, was obtained as a characteristic material constant, dependent only on the molecular weight of the high polymer and its absolute value for inhomogeneity.

It is the hope of the authors that scientific practice for characterizing high polymers will increasingly refer to the flow behavior of (their) solutions by determining the flow curve.

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## EVALUATION OF RUBBER-SOLVENT INTERACTION \*

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It is known that the solution (or swelling) of rubbers is accompanied by a decrease in the free energy  $\Delta F$  of the rubber-solvent system

$$\Delta F = \Delta H - T\Delta S \quad (1)$$

where  $\Delta H$  is the enthalpy change;  $\Delta S$  is the entropy change, and  $T$  is the absolute temperature.

If  $F$  decreases continuously during the swelling, the result is unlimited swelling or solution. If  $F$  passes through a maximum with increase of swelling, the swelling is limited. This latter case is characteristic of vulcanizates.

The equilibrium swelling can be theoretically calculated from the Flory<sup>1</sup> equation:

$$\ln \left( 1 + \frac{1}{Q_\infty} \right) - (Q_\infty + 1)^{-1} - \mu(Q_\infty + 1)^{-2} - \frac{1}{m_e} [(Q_\infty + 1)^{-1} - \frac{1}{2}(Q_\infty + 1)^{-2}] = 0, \quad (2)$$

where  $Q_\infty$  is the equilibrium degree of swelling, expressed as the ratio of the volume increase of the swollen specimen to the volume of the dry specimen after swelling;  $m_e = M_r/\rho_r V_s$ ;  $V_s$  is the molar volume of the solvent in cubic centimeters per mole;  $\rho_r$  is the density of the rubber in grams per cubic centimeter;  $M_r$  is the molecular weight of a segment of the molecular chain between adjacent crosslinks;  $\mu$  is a parameter characterizing intermolecular interaction between the rubber and the solvent. Two other equations<sup>2,3</sup> are known which connect  $Q_\infty$  with the density of the vulcanization network and a parameter characterizing rubber-solvent interaction. However, Equation (2) is the one most commonly used.

The enthalpy increment  $\Delta H$  on mixing increases with increasing  $\mu$ . The intermolecular interaction parameter  $\mu$  depends on the ratio of the square roots of the cohesive energy densities for the rubber and the solvent<sup>4,5</sup>.

$$\mu = \mu_s + \frac{V_s(\delta_r - \delta_s)^2}{RT} \quad (3)$$

where  $\delta_r$  and  $\delta_s$  are the square roots of the cohesive energy densities of the rubber and solvent, respectively. These are generally known<sup>4,5</sup> as the solubility parameters. The value of the parameter for the solvent can be calculated

\* Reprinted from *Colloid Journal* 19, 375-382 (1957); an English translation by Consultants Bureau, no. of *Kolloidnyi Zhurnal* 19, 376-383 (1957).

from its latent heat of vaporization ( $\Delta H_v$ ) at the given temperature:

$$\delta_s = \sqrt{\frac{\Delta H_v - RT}{[V_s]}}, \quad (4)$$

in Equation (3)  $\mu_s = 1/\gamma$ , where  $\gamma$  is the number of solvent molecules surrounding one segment of the rubber molecule. It is generally assumed that  $\gamma$  is constant for all rubbers<sup>5</sup>. On the basis of literature data it is assumed in the present paper that  $\gamma = 4$ .

TABLE I  
VALUES OF THE SOLUBILITY PARAMETER  $\delta$  IN (CAL/CC)<sup>1/2</sup> FOR  
VARIOUS RUBBERS

Rubber	Literature data		Calculated
	Gee <sup>3</sup>	Scott <sup>4</sup>	
NR	7.98	8.35	8.22
Sodium polybutadiene	—	8.45	8.35
SBR, 15% styrene (Buna S type)	—	8.55	—
SBR, 25%	8.1	8.60	8.45
SBR, 40%	—	8.70	—
Polychloroprene (GN type)	8.2	9.25	9.00
NBR (Buna N type)	—	9.50	9.70

We must point out that Equation (3) is valid for systems with the same nature of intermolecular interaction forces (for example, nonpolar rubber-nonpolar solvent). Equation (2) shows that the interaction of solvents with rubbers and vulcanizates depends on the absolute values of  $\mu$  and  $m_c$ . It should be noted that the parameter  $\mu$  depends on the chemical nature of the rubber units and is independent of the molecular weight of the polymer, and therefore it characterizes the interaction both of the rubber itself and of its vulcanizates with the solvent.

TABLE II  
RANGE OF SOLUBILITY PARAMETERS FOR SOLVENTS OF DIFFERENT CHEMICAL  
CLASSES, CALCULATED FROM THE HEATS OF VAPORIZATION AT 25°

Solvents	Range of values of $\delta$ (cal/cc) <sup>1/2</sup>
Paraffin hydrocarbons	6.75*– 7.55
Low molecular aromatic hydrocarbons	9.15 – 8.80
Ethers	7.90 – 7.45
Esters	10.15 – 8.00
Ketones	9.9 – 7.6
Nitriles	11.9 – 9.4
Monohydric alcohols	16.5 – 10.3

\* The values of  $\delta$  on the left refer to solvents of lower molecular weight.

It has been shown in a number of investigations<sup>6,7</sup> that for limited swelling of unvulcanized rubber,  $\mu > 0.5$ . Therefore, for a rough evaluation of the solvent power of a particular solvent it is sufficient to compare the values of the solubility parameters for the rubber and the solvent.

Values of the solubility parameters of certain rubbers and solvents, taken from the literature and calculated, are given in Tables I and II.

It follows from Equation (3) that the value of  $\mu$  decreases, and the solvent power of a given solvent therefore increases, with decreasing absolute difference

between the solubility parameters of the rubber and the solvent. However, some classes of solvents, such as hydrocarbons, ethers, and ketones, may have similar solubility parameters (Table II) but different solvent powers; i.e., Equation (3) is not applicable to the general case of solution of rubbers in different solvents. Gu<sup>18</sup> showed that this is because Equation (3) does not take into account the differences in the intermolecular forces acting between different rubbers and solvents. Some authors<sup>4</sup> propose the introduction of a correction factor  $K > 1$  into Equation (3) for describing the interaction of rubbers with different solvents

$$\mu = \mu_s + \frac{K \cdot V_s (\delta_r - \delta_s)^2}{RT} \quad (5)$$

The factor  $K$  is to be calculated from experimental values of  $\mu$  found with the aid of Equation (2) from the degrees of swelling of the same vulcanizate in different solvents. However, this calculation method is laborious and is valid for only a few solvents. In the present paper a method is proposed for graphical determination of  $\mu$  from Equation (5), applicable to the interaction of a number of rubbers with solvents of different chemical classes. Since the correction factor  $K$  takes differences in the nature of the intermolecular forces into account, it is to be expected that  $K$  will have the same value for a given rubber and solvents of the same chemical nature.

We write Equation (5) in the form:

$$\delta_s = \delta_r \pm \sqrt{RT/K} \cdot \sqrt{(\mu - \mu_s)/V_s} \quad (6)$$

For systems with intermolecular interaction forces of the same character  $RT/K = \text{const}$ . Therefore for such systems Equation (6) represents a linear relationship between  $\sqrt{(\mu - \mu_s)/V_s}$  and  $\delta_s$ . A line of this type cuts off an intercept numerically equal to the solubility parameter  $\delta_r$  of the rubber along the ordinate axis.

Data on the swelling of filled and unfilled vulcanizates in a large number of solvents<sup>4,5,9-12</sup> (the solvents are listed in Table III) were used to calculate values  $\sqrt{(\mu - \mu_s)/V_s}$  from Equation (2). The values so found were plotted graphically (Figures 1-5). It was found that the parameter  $\mu$ , characterizing intermolecular interaction, is independent of the loading of the rubber. Figure 1 shows points for the swelling of three different filled and three unfilled natural rubber vulcanizates in about 50 solvents. Figure 2 gives data for swelling of three butadiene-styrene rubbers (SBR) containing 25% styrene (Buna S type) in 28 solvents, and Figure 3, for three polychloroprene rubbers (Neoprene GN type) in 25 solvents. Figure 4 refers to swelling of one sodium butadiene rubber in 7 solvents, and Figure 5, to one NBR rubber (Buna N type) in 9 solvents.

The graphs show that all points corresponding to systems with intermolecular interaction of the same character lie on one straight line. Several lines intersect at one point, thus determining the exact value of the solubility parameter of the given rubber (Table I).

The accuracy with which the position of the straight lines determining the interaction of rubbers with solvents of different chemical classes is fixed increases with increasing amounts of experimental data used for plotting these graphs (for example, 115 points were plotted for natural rubber in Figure 1).

It is seen in Figure 1 that the points corresponding to saturated and aro-

matic hydrocarbons lie along one straight line. The points for all the ketones, esters, and ethers given in Table III also lie on one straight line. The behavior of alcohols is different.

In the action of alcohols on natural rubber the nature of the intermolecular interaction changes with increasing molecular weight of the alcohol. As a re-

TABLE III

LISTS OF SOLVENTS USED IN CALCULATIONS OF THE  $\delta_s - \sqrt{(\mu - \mu_s)/V_s}$   
RELATIONSHIPS SHOWN IN FIGURES 1-5

Symbol on  
graph\*

Solvents

Fig. 1, natural rubber

NR-I	Saturated and aromatic hydrocarbons
NR-II	Methyl ethyl ketone, diisopropyl ketone, mesityl oxide, methyl formate, diethyl ether, ethyl acetate, <i>n</i> -amyl acetate, propyl acetate, <i>n</i> -butyl acetate, <i>n</i> -butyl <i>n</i> -butyrate, isobutyl <i>n</i> -butyrate, limonene, isoprene, butyraldehyde, acetone
NR-IIIa	Nitriles; alcohols: tertiary butyl, amyl, <i>n</i> -propyl; nitromethane
NR-IIIb	Dioxane, chloroform; alcohols: hexyl, benzyl
NR-IIIc	Alcohols: heptyl, octyl; cyclohexane, dichloroethane, carbon tetrachloride, styrene, acetyl chloride, nitrobenzene

Fig. 2, butadiene—styrene rubber

BSK-I	Saturated and aromatic hydrocarbons; limonene, dichloroethane, carbon tetrachloride
BSK-II	Cyclohexane, cyclohexene, methyl ethyl ketone, mesityl oxide, ethyl acetate, <i>n</i> -amyl acetate
BSK-III	Styrene, chloroform, dioxane, carbon disulfide, benzyl alcohol
BSK-IV	Isoprene, methylcyclohexane, ethyl ether, hexyl alcohol, octyl alcohol, acetone

Fig. 3, polychloroprene

A-1	Benzene, toluene, methyl ethyl ketone, ethyl formate, methyl acetate, ethyl acetate, <i>n</i> -propyl acetate
A-2	<i>n</i> -Pentane, <i>n</i> -hexane, <i>n</i> -heptane
A-3	Chloroform, carbon tetrachloride, dichloroethane, xylene, methyl formate, <i>n</i> -butyl acetate, acetone
A-4	Dioxane, aniline, ethyl ether, hexyl alcohol
A-5	Nitrobenzene, diisopropyl ketone, <i>n</i> -butyl <i>n</i> -butyrate, isobutyl <i>n</i> -butyrate

Fig. 4, sodium butadiene rubber

SKB-1	<i>n</i> -Hexane, <i>n</i> -heptane, benzene, toluene, <i>p</i> -xylene, ethylbenzene, carbon tetrachloride
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Fig. 5, butadiene—acrylonitrile rubber

SKN-1	<i>n</i> -Hexane, <i>n</i> -heptane, cyclohexane, benzene, toluene, <i>p</i> -xylene, ethylbenzene, chloroform, carbon tetrachloride
-------	--

\* NR means natural rubber, BSK styrene butadiene rubber, SKN acrylonitrile butadiene rubber, and SKB butadiene rubber.

sult, the points corresponding to swelling of NR vulcanizates in tertiary butyl, amyl, and *n*-propyl alcohols lie on one straight line, and the points for *n*-heptyl and *n*-octyl alcohols on another.

Of the data used, only the point for the interaction of NR with cyclohexane did not lie on one of these lines for NR. The interaction of polychloroprene rubbers with solvents could not be represented by straight lines specific for given homologous series. Points representing interaction of polychloroprene

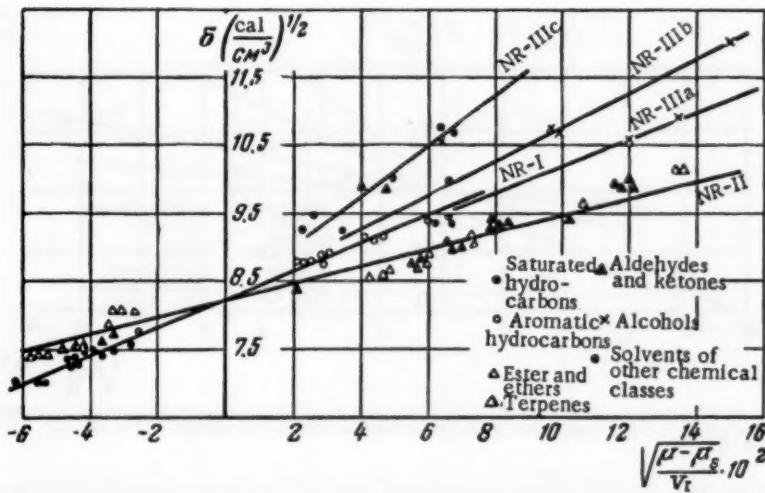


FIG. 1.—Variation of  $\delta_r$  with  $\sqrt{(\mu - \mu_s)/V_s}$  for natural rubber;  $\delta_r = 8.22$  (cal/cc)<sup>1/2</sup>;  $\mu_s = 0.25$ .

rubbers with different esters or ethers lay on different lines. The regular transition from one line to another, found for the swelling of NR in alcohols, is not shown in this case. The probable explanation is the insufficient accuracy of the data used. Further investigations are needed for a complete characterization of the behavior of polychloroprene.

The straight lines in Figure 1 can be used to evaluate the interaction of natural rubber not only with the solvents listed in Table III, but also with their

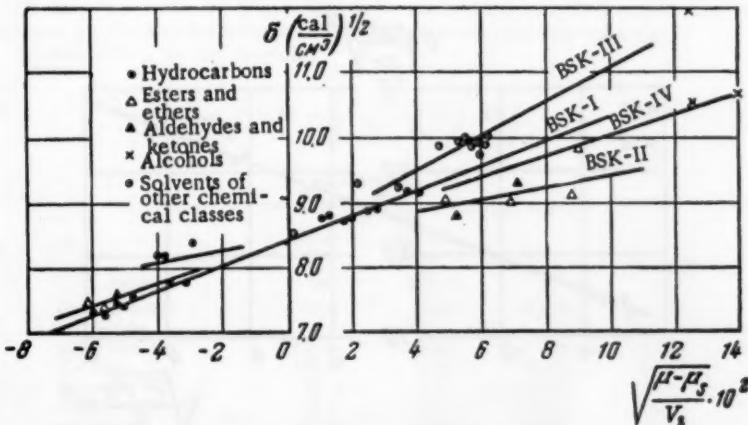


FIG. 2.—Variation of  $\delta_r$  with  $\sqrt{(\mu - \mu_s)/V_s}$  for SBR rubber with ~25% styrene;  $\delta_r = 8.45$  (cal/cc)<sup>1/2</sup>;  $\mu_s = 0.25$ .

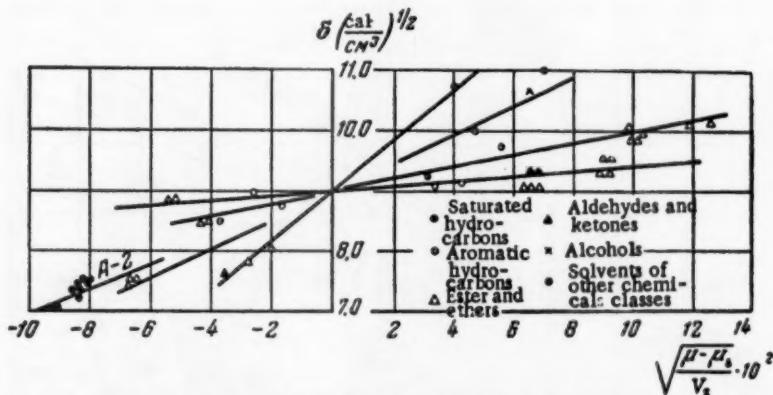


FIG. 3.—Variation of  $\delta_r$  with  $\sqrt{(\mu - \mu_s)/V_s}$  for chloroprene rubber of the Neoprene type;  $\delta_r = 9.00$  (cal/cc) $^{1/2}$ ;  $\mu_s = 0.25$ . Designations of the curves (reading downward on the right of the diagram): A-5, A-4, A-3, A-1.

homologs; the lines for polychloroprene (as given in Figure 3) can be used only for determining its interaction with the solvents given in Table III.

The data in Figure 3 show that for determination of the parameter  $\mu$  it is not always possible to make use only of the difference between the absolute values of the solubility parameters of the solvent and the rubber. For example, for ethyl formate the solubility parameter  $\delta_r = 9.43$  (cal/cc) $^{1/2}$ , for isobutyl *n*-butyrate  $\delta_r = 7.78$  (cal/cc) $^{1/2}$ , and for polychloroprene  $\delta_r = 9.00$  (cal/cc) $^{1/2}$ . It seems at first sight that polychloroprene should swell better in ethyl formate than in isobutyl *n*-butyrate, but it follows from Figure 3 that  $\mu$  for the system polychloroprene-ethyl formate is 0.95, and for the system polychloroprene-isobutyl *n*-butyrate it is 0.46, so that the solvent power of isobutyl *n*-butyrate is much greater.

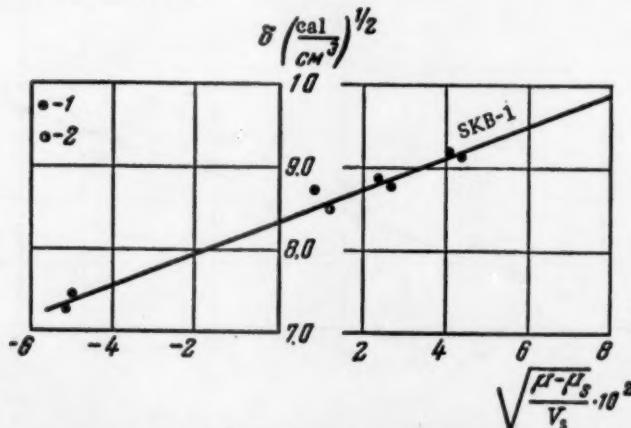


FIG. 4.—Variation of  $\delta_r$  with  $\sqrt{(\mu - \mu_s)/V_s}$  for sodium butadiene rubber SKB-I;  $\delta_r = 8.35$  (cal/cc) $^{1/2}$ ;  $\mu_s = 0.25$ : 1) hydrocarbons; 2) carbon tetrachloride.

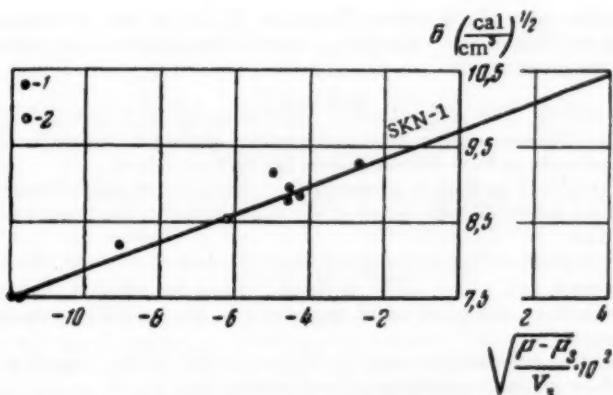


FIG. 5.—Variation of  $\delta_s$  with  $\sqrt{(\mu - \mu_s)/V_s}$  for divinyl-acrylonitrile rubber SKN-I of Buna N type;  $\delta_s = 9.70$  (cal/cc) $^{1/2}$ ;  $\mu_s = 0.25$ ; I) hydrocarbons; II) carbon tetrachloride.

Let us consider the swelling of vulcanized SKS-30 rubber (composition in parts by weight: rubber 100, sulfur 0.5, diphenylguanidine 0.3) in solvents of approximately the same molecular volume but with different types of intermolecular forces (Table IV).

It is seen from Table IV that the maximum swelling of the vulcanize decreases with increase of  $\mu$ , and that the different character of the intermolecular forces in *n*-amyl acetate and benzene leads to quite different values of  $\mu$  although the values of  $\delta_s$  for these solvents are approximately the same.

To determine the solvent power of a given solvent at normal temperature it is necessary to:

- 1) calculate  $\delta_s$  by means of Equation (4) from tabular data on heats of vaporization at 20–25°;
- 2) find the value of  $\sqrt{(\mu - \mu_s)/V_s}$  in one of the graphs (from a known ordinate on the line for solvents of the appropriate homologous series);
- 3) calculate  $\mu$  by the formula:

$$\mu = 0.25 + \left[ \left( \sqrt{\frac{\mu - \mu_s}{V_s}} \right)^2 \cdot V_s \right] \quad (7)$$

TABLE IV  
SWELLING OF SKS-30 RUBBER VULCANIZATES

Solvents	Molar volume in cc/mole	Solubility parameter $\delta_s$ in (cal/cc) $^{1/2}$	Parameter $\mu$	Maximum swelling $Q_{\infty}$
Carbon tetrachloride	96.5	8.50	0.250	41.0
<i>m</i> -Xylene	123.0	8.80	0.292	34.5
Toluene	107.0	8.90	0.312	34.6
Benzene	89.5	9.15	0.375	31.4
Dichloroethane	78.7	9.75	0.624	21.1
<i>n</i> -Heptane	146.0	7.45	0.648	6.91
<i>n</i> -Amyl acetate	147.0	9.10	0.912	3.30
Ethyl acetoacetate	127.0	10.00	1.550	0.30

When the value of  $\mu$  is known, Equation (2) can be used to determine the maximum swelling of any vulcanizate, with known density of the spatial network, in the given solvent.

#### SUMMARY

1. The influence of differences in the nature of the intermolecular forces in different solvents on their solvent powers has been examined.

2. A graphical method is proposed for evaluation of the influence of the nature of the intermolecular forces of the solvent on the maximum swelling of vulcanizates.

3. For a given rubber and a given chemical class of solvents, the relationship between  $\delta_s$  and  $\sqrt{(\mu - \mu_s)/V_s}$  is linear. Lines for different classes of solvents intersect at one point which represents  $\delta_r$ , the solubility parameter for the rubber.

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# BRANCHING IN MACROMOLECULES OF DIFFERENT SYNTHETIC RUBBERS \*

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## INTRODUCTION

Branching in macromolecules of synthetic rubbers is one of their most important structural properties, exerting a pronounced influence on the physical behavior of these materials. The degree of branching evidently depends on the chemical nature of the free radicals or organometallic catalyst initiating the polymerization reaction. It also depends on the conditions of the reactions, particularly on the polymerization temperature, as the latter determines the relative rates of the propagation and branching reactions. The problem of developing a general quantitative method for the determination of branching in the molecules of high polymeric substances cannot yet be considered as solved. This problem appears to be very complicated and only a few experimental data are available<sup>1</sup>. Therefore the development and application of methods with a sound physical background for the qualitative evaluation of branching have not lost their value.

Most methods used for the determination of branching are based on the relations existing between the dimensions of molecular coils in solution and the degree of branching. Certain limitations of the methods commonly used for the determination of branching by values of Huggins' constant  $K'$ , the thermodynamic parameter  $\mu$ , or the second virial coefficient arise from the fact that by such methods the above relation cannot be precisely accounted for. Therefore, in the present investigation, the degree of branching has been studied by viscosity measurements and also by determining the dynamo-optical properties of a polymer-fraction solution. The parameters found by this method, namely the dynamo-optical constant  $[\Delta n]$ , obtained from the magnitude of the flow birefringence, the rotational friction coefficient,  $W$ , calculated from the orientation angles, as well as the intrinsic viscosity  $[\eta]$ , all are determined by the dimensions of the molecular coils. By these methods, the investigation of the influence of the polymerization temperature on the branching for a number of synthetic rubbers obtained in the presence of different catalysts was carried out.

Moreover, the intrinsic viscosity determinations made it possible, by the use of modern theories of polymer solutions, to estimate quantitatively branching in molecules of some synthetic rubbers.

## MATERIALS USED AND EXPERIMENTAL DETAILS

The following samples of different rubbers have been examined: potassium-butadiene rubbers obtained by a vapor phase polymerization process at temperatures of 0 and 60°, sodium-butadiene rubbers prepared by polymerization in the liquid and vapor phase in a temperature range from 10 to 70°, lithium-is-

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prene rubbers obtained at temperatures of 55 and 85°, as well as emulsion butadiene-styrene rubbers (70/30), polymerized at temperatures of 50, 5, and -15°. The measurement of the flow birefringence magnitude  $\Delta n$  and of the extinction angle  $\varphi$  has been carried out in a dynamo-optimer with an internal rotor as described by Tsvetkov<sup>2</sup> at velocity gradients of 800 to 15,000 sec<sup>-1</sup> and a temperature of 25 ± 0.02° with the use of an optical scheme with a compensating plate  $\delta = 0.048$ . The values of  $\Delta n$  and  $\varphi$  of polymer fraction solutions in benzene have been determined at different velocity gradients  $G$  and concentrations  $C$ ; from the plots of  $\Delta n$  and  $\varphi$  against  $G$  the values of  $\Delta n/GC$  and  $\varphi/G$  at  $G \rightarrow 0$  have been computed.

In order to estimate the characteristic birefringence values

$$[\Delta n] = \lim_{\substack{G \rightarrow 0 \\ C \rightarrow 0}} \frac{\Delta n}{GC}$$

we made use of the extrapolation formula

$$[\Delta n] = \Delta n/GC\eta_0\sqrt{\eta_r}$$

The latter<sup>3</sup> has been shown to be valid for all the polymers investigated over a wide range of concentrations. The extrapolation of the initial slopes of the curves  $\varphi = f(G)$  to  $C \rightarrow 0$  could not be carried out. But, over the available range of concentrations, the  $W$ -values calculated according to the equation:

$$W = \frac{12\kappa T}{\eta} (\varphi/G)_{G \rightarrow 0}$$

have been shown to remain constant if the absolute viscosities  $\eta_0\eta_r$  are used for the viscosity coefficient. The  $W$ -values obtained by the above method have been used in the present study. For the determination of the intrinsic viscosity  $[\eta]$  of benzene solutions, the Ostwald viscometer for volatile solvents has been chosen; the choice of its dimensions has been made in such a way that the correction for kinetic energy could not exceed 0.4%.

The molecular weight determination of polymer fractions has been carried out by the osmotic method with a modified osmometer of the Fuoss and Mead type<sup>4</sup>.

Fractionation was carried out by a fractional precipitation from dilute benzene solutions with methanol as precipitant; the special conditions for the forming of homogeneous fractions being kept carefully<sup>5,6</sup>.

## RESULTS AND DISCUSSION

At equal molecular weight values, the macromolecules of branched polymers are known to occupy, in solutions in a given solvent, a smaller volume than linear molecules of the same chemical structure. Therefore, in such cases, regardless of the model of branching, the magnitude of flow birefringence, the rotational friction coefficient, and the intrinsic viscosity should have lesser values in branched polymers than in linear or less branched polymers. It could be mentioned that the relative content of 1,2,3,4 and *cis-trans*-1,4 addition configurations in the molecular chain also influences the dimensions of the molecular coil in solution, though to a lesser extent<sup>7,8</sup>. This fact ought to be considered when interpreting the corresponding data. The results of investigating dyna-

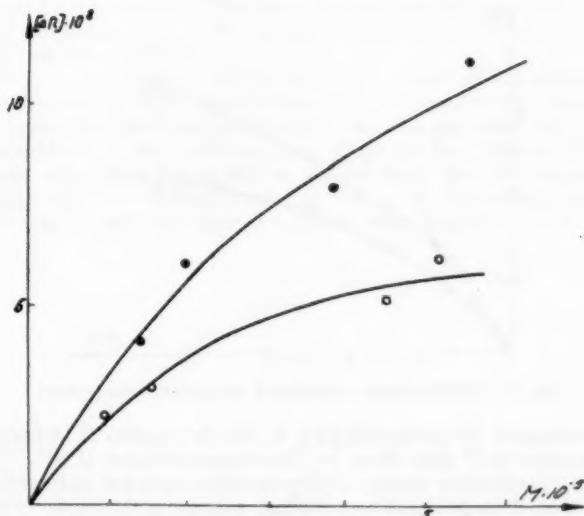


FIG. 1.—Dynamo-optical constants of fractions of potassium-butadiene rubbers.  
Top curve: 0°. Bottom curve: 60°.

mo-optical and viscous properties of homogeneous fractions of potassium-butadiene rubber samples obtained by polymerization at 0 and 60° are shown in Figures 1, 2, and 3. It follows that, throughout the range of molecular weight

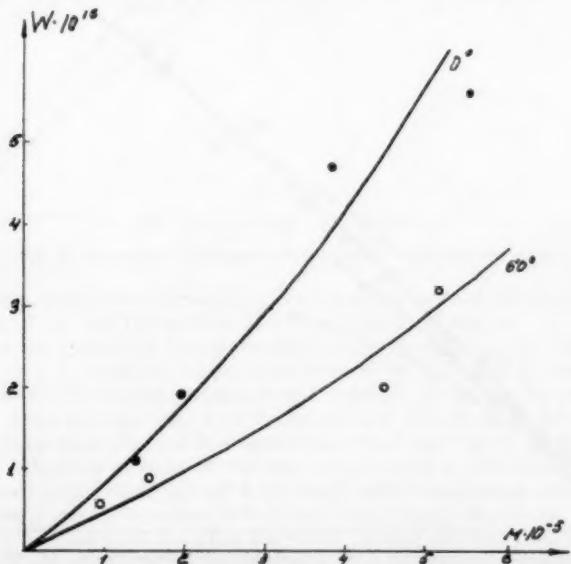


FIG. 2.—Rotational friction coefficients of fractions of potassium-butadiene rubbers.

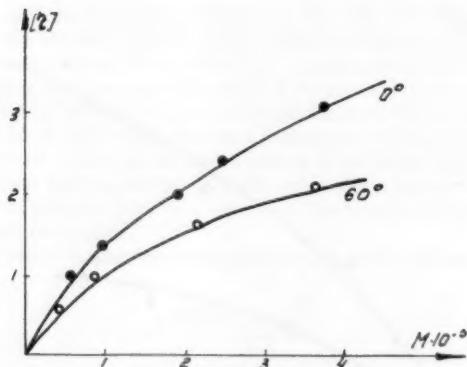


FIG. 3.—Intrinsic viscosity of fractions of potassium-butadiene rubbers.

values investigated, the curves of  $[\Delta n]$ ,  $W$ , and  $[\eta]$  against  $M$  lie higher for the sample obtained at  $0^\circ$  than those for the sample obtained at  $60^\circ$ . Thus, the increase in temperature during the potassium-catalyzed polymerization of butadiene from  $0^\circ$  to  $60^\circ$  leads to a marked increase in the degree of branching (the microstructures of these polymers, as determined by infrared spectroscopy,

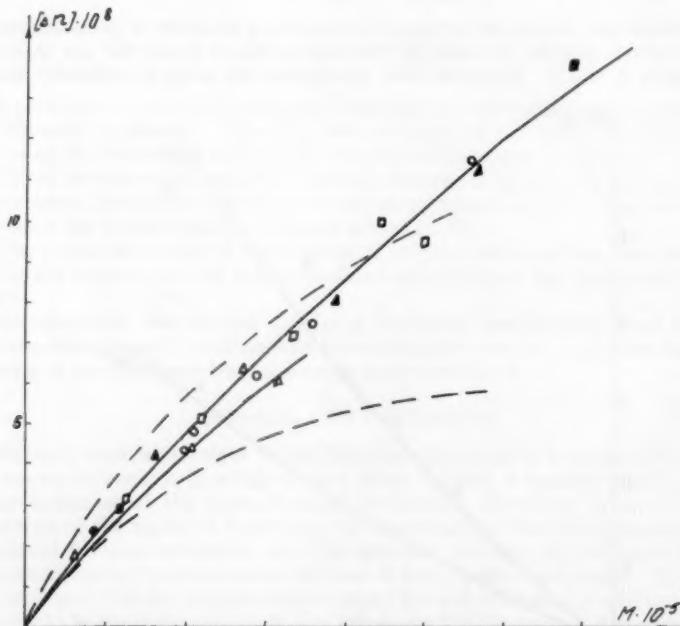


FIG. 4.—Dynamo-optical constants of fractions of sodium-butadiene rubbers. (○, □, Δ) Samples obtained in a vapor phase at 20, 40, and 60°. (●, ■, ▲) Samples obtained in a liquid phase at 10, 20, and 70°. The dashed lines represent the curves for the potassium-butadiene rubbers.

are practically identical<sup>9</sup>. Therefore, the potassium-butadiene rubber obtained by polymerization at 60°, being a highly branched polymer, has low tensile and elastic properties.

It follows from Figure 4, which shows the values of the dynamo-optical constants of sodium-butadiene rubber samples prepared at temperatures from 10 to 70°, that the function  $[\Delta n] = f(M)$  may be expressed for most of the polymers studied by one common plot. Only for the polymer obtained by vapor phase polymerization at 60° do the values of  $[\Delta n]$  lie somewhat lower than the general curve (usually when this method of polymerization is used the temperature in the polymer mass exceeds to a considerable extent the tempera-

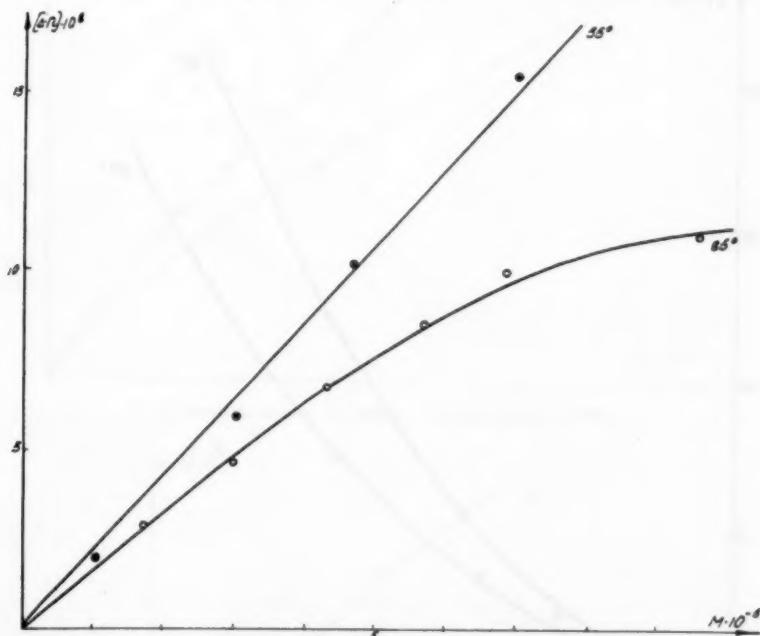


FIG. 5.—Dynamo-optical constants of fractions of lithium-isoprene rubbers.

ture of the bath mentioned above). The functions  $[\eta] = f(M)$  and  $W = f(M)$  are identical for all the sodium-butadiene polymers studied. It should be noted that an increase in polymerization temperature from 10 to 70° leads in this case to a decrease in 1,2-addition from 80 to 64% and a corresponding increase in the cis-1,4-configuration from 3 to 20%. However, according to the estimate of the authors cited above<sup>7</sup>, the changes in molecular coil dimensions resulting from these changes in structure are small and nearly compensate one another. Thus, an increase in reaction temperature in the sodium-catalyzed polymerization of butadiene over a relatively wide temperature range does not bring about a marked increase in the branching of macromolecules.

It may be concluded from the above results that the character of the temperature effect on the branching degree in the preparation of butadiene poly-

mers in the presence of alkali metals depends on the nature of the catalyst used. The greater influence of the polymerization temperature on the branching of potassium-butadiene rubbers is in accordance with the known tendency for metallation reactions to increase in the order: lithium < sodium < potassium. On the other hand, an increase in branching, as shown by the data of Figures 5, 6, and 7, may also be noted for lithium-catalyzed isoprene polymerization at high temperatures (the polymers studied did not differ in respect to micro-structure). This cannot be due to metallation reactions, as organolithium compounds show a much smaller tendency for metallation reactions than other

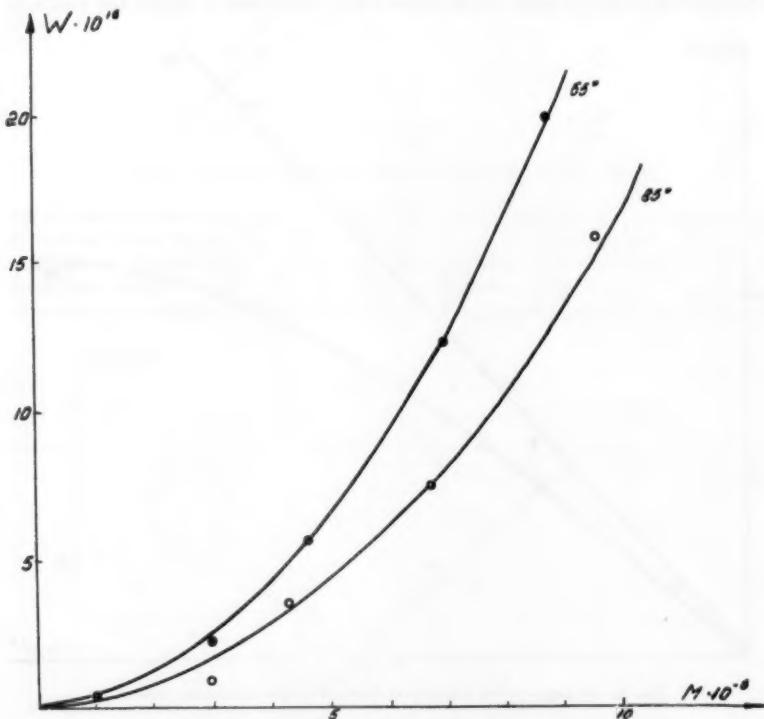


FIG. 6.—Rotational friction coefficients of fractions of lithium-isoprene rubbers.

alkali metallorganic compounds, but, in accordance with the results reported by Korotkov and Nikolaev<sup>10</sup>, this seems to be connected with the fact that the addition of organolithium compounds to the polymer double bonds becomes very appreciable at higher temperatures.

The values of the dynamo-optical constant for fractions of butadiene-styrene emulsion polymers prepared at different temperatures are shown in Figures 8 and 9. The curve  $[\Delta n] = f(M)$  characterizing the polymer obtained at  $5^\circ$  lies above the corresponding curve for the higher temperature sample and does not differ from the curve for sample of the  $-15^\circ$  polymer. The function  $[\eta] = f(M)$  is shown to be practically identical for all the polymers investigated.

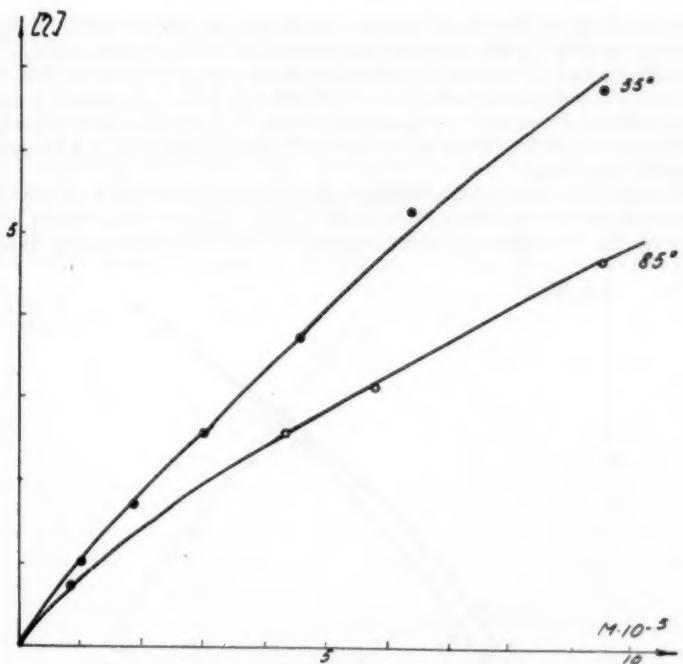


FIG. 7.—Intrinsic viscosity of fractions of lithium-isoprene rubbers.

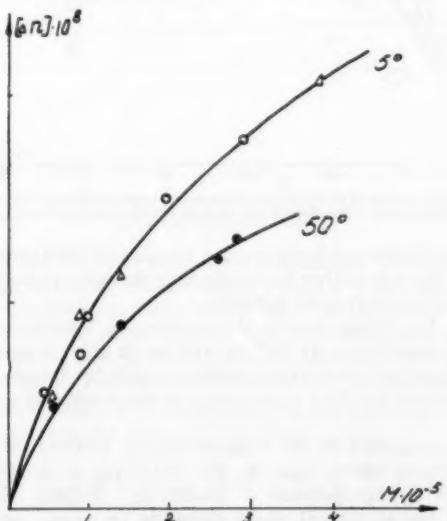


FIG. 8.—Dynamo-optical constants of fractions of butadiene-styrene rubbers.

Thus, according to the above results, a reduction of polymerization temperature from 50 to 5° in the emulsion polymerization of a butadiene-styrene mixture initiated by free radicals seems to bring about a slight decrease in branching. A further temperature reduction to -15° does not have any marked influence on the molecular structure. Figure 9 shows also that an increase in conversion, reaching about 100% in this reaction at -15°, does not give rise to a measurable change in branching.

The specific nature of the polymerization temperature effect on branching in macromolecules of different synthetic rubbers has thus been shown by the above results. It should be mentioned that a method of comparing dynamo-

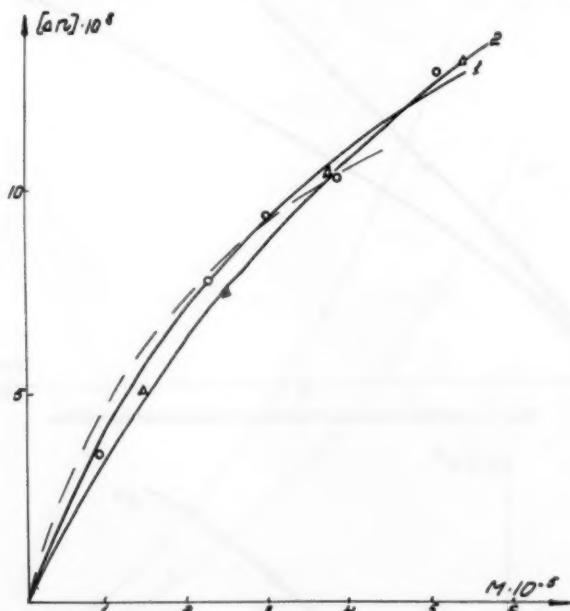


FIG. 9.—Dynamo-optical constants of fractions of butadiene-styrene rubbers obtained at -15°. (1) 60% and (2) 100% conversions. The dashed line represents the curve for a sample obtained at 5°.

optical constants of polymer fractions in a number of instances proved to be, as it was expected, more sensitive for evaluating the relative degree of branching than the viscosity measurement method.

For instance, the higher degree of branching in butadiene-styrene rubbers obtained by polymerization at 50° as well as in high temperature, sodium-catalyzed butadiene polymerization products could be detected neither by viscosity determinations nor by a comparison of the constants  $\mu$  and  $K'$  for polymer fractions.

This greater sensibility of the dynamo-optical method seems to arise from an additional optical effect, namely, the reduction in optical anisotropy of molecules caused by an increase of branching. Indeed, the differences in polarizability of the statistical chain elements ( $\alpha_1 - \alpha_2$ ), as evaluated from the ratio  $[\Delta n]/[\eta]$  in Kuhn's equation<sup>11</sup>, equal  $46 \times 10^{-25}$  cm for low tempera-

ture sodium and potassium polymers, respectively, and  $43 \times 10^{-25}$  cm and  $41 \times 10^{-25}$  cm, respectively, for the same rubbers obtained by polymerization at  $60^\circ$ . For butadiene-styrene rubber samples obtained at  $50^\circ$  and  $5^\circ$ , the values of  $(\alpha_1 - \alpha_2)$  are  $45 \times 10^{-25}$  cm and  $60 \times 10^{-25}$  cm, respectively.

At the same time, with the present state of our theoretical knowledge, it is on the basis of intrinsic viscosity measurements quantitative data on the degree of branching can be obtained. In the case of solvent-impermeable molecular coils, the ratio of intrinsic viscosities of branched ( $[\eta]_b$ ) and linear macromolecules in an ideal solvent ( $\theta$ -solvent) is known to be equal to the ratio of the third powers of their unperturbed linear dimensions. However, the direct use of this simple relationship may be possible only in those few instances in which

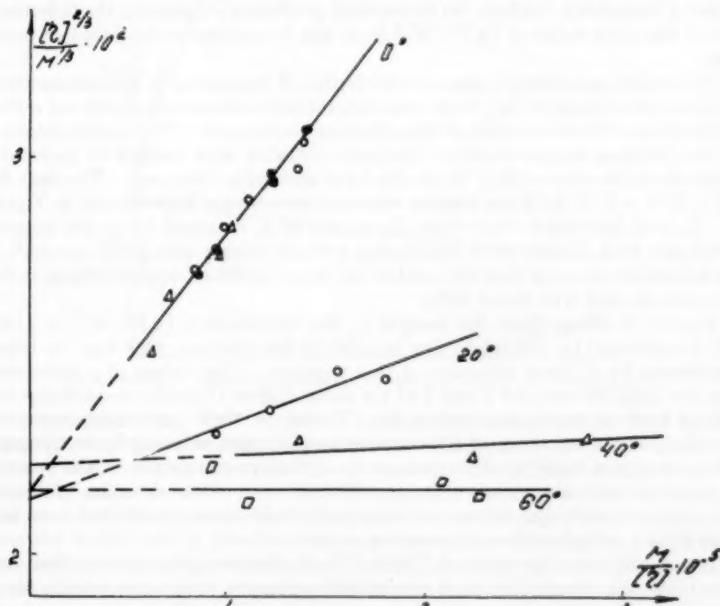


FIG. 10.—A plot of  $[\eta]^{2/3}/M^{1/3}$  against  $M/[\eta]$  for benzene solution fractions of potassium-butadiene rubbers.

a strictly linear polymer of the same type is available. This difficulty may be overcome if, as suggested by Wales<sup>12</sup>, Flory's theory is also applied to branched polymers. The intrinsic viscosity would then be expressed by the equation  $[\eta] = KM^{1/2}\alpha^3g^{3/2}$  where  $g = r_{\beta 0}^2/r_0^2$  is the ratio of mean square radii for branched and linear molecules in an ideal solvent,  $\alpha$  is the increase of the linear dimensions of a molecule due to the intermolecular interaction polymer-solvent molecules, and  $K = \Phi'(r_0^2/M)^{3/2}$  where  $\Phi' = 14.7\Phi$  and  $\Phi$  is the universal Flory's constant.

The analysis leads to the following relation:

$$\frac{[\eta]^{2/3}}{M^{1/3}} = gK^{2/3} + 2C_m\psi_1 [1 - (\theta/T)] \left( \frac{M}{[\eta]} \right) K^{5/3}g^{5/2}$$

The values  $C_m$  and  $\psi_1$  are the corresponding parameters in Flory's theory.

According to the last equation, the limit value of  $[\eta]^{2/3}/M^{1/3}$  at  $M \rightarrow 0$  does not depend on the degree of branching of the molecules and equals  $K^{2/3}(g \rightarrow 1)$  at  $M \rightarrow 0$ . The value of  $g$  for fractions of any molecular weight, if  $[\eta]$  is measured in an ideal solvent, may be found by using the relation:  $g = [\eta]_{[\eta]}^{2/3}/MK^{2/3}$ .

The data of Figure 10, showing the relationship

$$\frac{[\eta]^{2/3}}{M^{1/3}} = f\left(\frac{M}{[\eta]}\right)$$

in benzene as applied to our potassium-catalyzed butadiene polymers differing in degree of branching, confirm the theoretical prediction concerning the independence of the limit value of  $[\eta]^{2/3}/M^{1/3}$  from the branching in the polymer molecules.

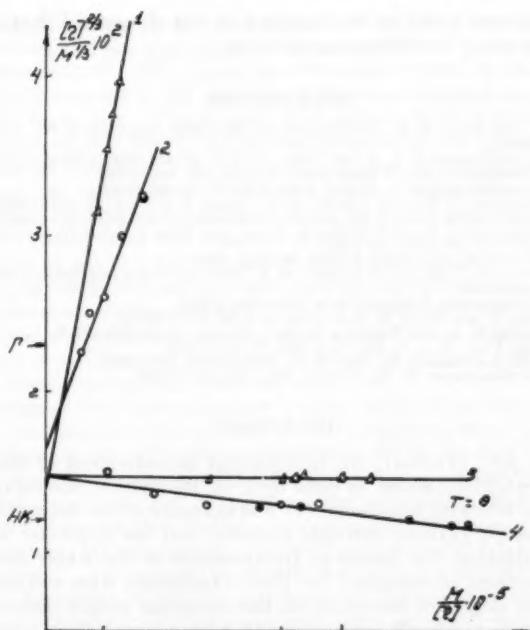
To obtain quantitative data on the degree of branching in lithium-isoprene polymers, the values of  $[\eta]$  have been determined in an ideal solvent for different fractions of three samples of the polymers mentioned. The results obtained on precipitation temperatures of fractions differing with respect to molecular weight show dioxane at 31.5° to be the ideal solvent in this case. The data for  $[\eta]^{2/3}/M^{1/3} = f(M/[\eta])$  for lithium-isoprene rubbers are represented in Figure 11. It is of interest to note that the values of  $K$  obtained by us are in good agreement with Flory's data concerning natural rubber and gutta percha<sup>12</sup>, if it is taken into account that the content of *cis*-1,4 addition configurations in the polymers studied was about 55%.

Figure 11 shows that, for sample 1, the relationship  $[\eta]^{2/3}/M^{1/3} = f(M/[\eta])$  is expressed by a straight line parallel to the abscissa; this may be taken as evidence for a linear structure of this polymer. The values of  $g$  calculated from the data for samples 2 and 3 of the same Figure 11 really characterize the ratio of hydrodynamic molecule radii. Therefore, these have been corrected according to the equation of Stockmayer and Fixman relating hydrodynamic and mean square radii<sup>14</sup> in order to make quantitative calculations of the branching possible from the values of  $g_{corr}$ . With the use of the equation of Stockmayer and Zimm<sup>15</sup>, the number of branch units in one molecule has been calculated for a tetrafunctional branching model.

It follows from the data of Table I that, for the polymers studied, one branching unit occurs for about every 4000 monomer units over a wide range of molecular weight values. The relatively high values obtained by us suggest that the polymers studied contain, not only tetrafunctional branch units, but also appreciable quantities of trifunctional ones, the latter being due to addition reactions to the polymer double bonds and possibly to metallation reactions.

#### SYNOPSIS

From results of a study of the intrinsic viscosity and the dynamo-optical properties of homogeneous polymer fraction solutions, the influence of the polymerization temperature on the degree of branching in various synthetic rubbers was determined. The dynamo-optical method proved to be the most suitable for our purpose. It was found that the influence of the polymerization temperature on the degree of branching of rubber macromolecules prepared in the presence of sodium, potassium, and lithium depends largely on the metal employed. With sodium-butadiene rubbers, even a considerable change in the temperature of polymerization has little influence on the degree of branching of

FIG. 11.—Plot of  $[\eta]^\frac{1}{M} / M^\frac{1}{2}$  against  $M/[\eta]$  for fractions of lithium-isoprene rubbers.

the macromolecules. On the other hand, when potassium is used as the catalyst, an increase in the polymerization temperature leads to a marked increase of the degree of branching. A considerable increase in the degree of branching was also observed in high-temperature, lithium-catalyzed polymerization. A relatively small effect of temperature on the degree of branching was observed in the case of butadiene-styrene copolymers obtained by free radical-initiated emulsion polymerization. The determination of the intrinsic viscosity of polymer fractions of various molecular weights in an ideal ( $\theta$ ) solvent permits a quantitative evaluation of the degree of branching by applying Flory's equation, as modified for the case of branched polymers. Such an evaluation was made for three samples of lithium-isoprene polymers. For two

TABLE I  
BRANCHING IN MOLECULES OF LITHIUM-ISOPRENE RUBBER FRACTIONS

$M \times 10^{-4}$	$\theta$	$\theta_{corr.}$	$\beta$	Relative branching $M/m\beta \times 10^{-4}$ $m = 68$
85	0.95	0.80	0.6	2.1
270	0.89	0.77	1.5	2.6
359	0.89	0.77	1.5	3.5
416	0.89	0.77	1.5	4.0
422	0.90	0.79	1.4	4.4
616	0.82	0.67	2.4	3.8
745	0.81	0.65	2.7	4.1
830	0.81	0.64	2.8	4.4

samples which were found to be branched, it was discovered that one branch unit occurs for every  $\sim 4000$  monomer units.

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### DISCUSSION

C. MUSSA I.V. (*Torino*): An independent measurement of the degree of branching of macromolecules, as done by Prof. Poddubnyi, should enable us to investigate the following questions: (1) The influence of the degree of branching on the relationship between intrinsic viscosity and the molecular weight; and (2) the investigation (by means of fractionation of the whole samples from which the fractions investigated by Prof. Poddubnyi were obtained) of the influence of the degree of branching on the molecular weight distribution.

It is known from Flory's calculations that branching arising from polyfunctional groups causes a narrowing of the differential weight distribution curve; on the contrary, branching through chain transfer, according to Beasley's calculations, must produce a broadening of this distribution.

I. YA. PODDUBNYI (*Leningrad*): At the present time it is difficult to estimate the influence of the degree of branching of macromolecules on the magnitude of volume effects, and therefore on the exponent  $a$  in the equation  $[\eta] = kM^a$ , not mentioning that new theories of viscosity of solutions assume the above relation of  $[\eta]$  to  $M$  only as an approximation in a limited range of  $M$ . Thus the use of data on small changes of  $a$  seems less convincing to me than direct comparison of the curves  $[\eta] = f(M)$ , for given polymers in a given solvent, since for any model of branching the magnitude of  $[\eta]$  of fractions of the same molecular weight will be less for the branched polymer. As far as the relation of the distribution curves to the degree of branching of molecules is concerned, such data were measured and I presented them at the All-Union Conference on Macromolecular Compounds in Moscow in February 1957. According to these data, the more branched polymers have wider distributions, and especially there is present a long high-molecular "tail."

H. EISENBERG (*Rehovot*): I would just like to draw the attention of Professor Poddubnyi to work by Zimm of about 5 years ago, where the branching of styrene was calculated and experimentally verified by the plot  $\log [\eta]$  against  $\log \bar{M}_w$ . It was found that  $a$  of course changed with molecular weight. Characteristic plots were obtained for linear and for branched chains. From the relationship between the two plots it was possible to derive a theory of the branching of molecules. This was verified by synthesizing the same type of molecules as linear and with a controlled degree of branching.

H. BENOIT (*Strasbourg*): Do you think that branching has no influence on the precipitation and the separation in the sample?

I. YA. PODDUBNYI: The question of Professor Benoit is hard to answer. We were very interested in the question of the dependence of fractionation on the degree of branching. The fractionation process is, as is known, based on the dependence of the critical conditions of solubility on molecular weight. The question of obtaining a homogeneous fraction is closely related to the methods used for that purpose. By means of an ultracentrifuge we have shown with Prof. Bressler that our fractions are homogenous and their coefficient of dispersion usually does not exceed 0.18–0.15. Practically nobody has followed the dependence of solubility on the degree of branching. Therefore it is possible that given individual fractions contain macromolecules of somewhat different molecular weights due to a different degree of branching. But the small values of the coefficient of dispersion which I have demonstrated show that the part of a differently branched molecule of another molecular weight included in the given fraction is not too large.

In the range of very high molecular weights, more of the branched material is present. We assumed this because of the presence of that high molecular "tail," and because the curve of the dependence of  $[\Delta n]$  and  $[\eta]$  on molecular weight has, in the range of very high molecular weights, a somewhat anomalous course. This may mean that in this range the separation occurs not only according to molecular weights, but also according to branching.

H. EISENBERG: Melville has studied the dependence of the degree of branching on conversion. He was able to show that at very low degrees of conversion the degree of branching is very low and increases exponentially when very high conversions are obtained. If this was investigated for polystyrene or polyvinyl acetate, much higher branching was obtained for the polyvinyl acetate and the curve increased much more rapidly for the latter polymer. So obviously, for studies of this kind, it is very important to study polymers produced at very low conversion (not more than 5%) where there is practically no branching in polystyrene, for instance, but there is already a reasonable amount of branching in polyvinyl acetate. On the other hand, the polyvinyl acetate is a very useful polymer for studies in branching because by hydrolysis of the acetate groups and by reacetylation one can get rid of the branches which are introduced in the molecule by chain transfer.

I. YA. PODDUBNYI: The dependence of branching on the degree of conversion results from the mechanism of polymerization and also dependence on the polymerization conditions which determine the velocity constants of the growth and branching. From the polymers which we investigated I will mention only the emulsion polymers. We found that conversion up to 60% has no influence upon the branching of the butadiene-styrene copolymer obtained at 5 and 50°. Higher conversions result in an increasing degree of branching. At –15° and in the presence of methanol the same system polymerizes up to a 100% conversion without an increase in the degree of branching. The reason is probably that 20% of the added methanol acts as a regulator. This is evidently connected also with the topography of polymerization; the polymer forms and deposits as a precipitate so that additional reactions do not take place.

## ADHESION OF HIGH POLYMERS. 3. EFFECTS OF THE SIZE, SHAPE, AND POLARITY ON ADHESION TO CELLOPHANE \*

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The effects of the nature of high polymers on their adhesive properties have been the subject of several investigations<sup>1-4</sup>. However, the question still remains obscure, as most of the investigations in this direction have been based on faulty methods. In particular, much harm was done in the earlier investigations because it was not strictly determined whether in the tests the joints were broken at the adhesive—substrate boundary or within the adhesive itself; i.e., whether true adhesion or the cohesive strength of the adhesive was being measured. Because of this, a number of experimental investigations of adhesion are rendered valueless, and the development of the physical chemistry of adhesion in general has been slow for this reason.

The present communication contains certain data on the effect of the nature of high polymer adhesives on adhesion to a polymeric substrate, obtained by means of a technique developed by us earlier<sup>5</sup>, in which the usual methodological defects have largely been eliminated. This method essentially consists of determination of the force or work expended in gradual peeling-off of a film of adhesive applied in solution form to the substrate. Special attention is paid to determining whether the peeling is adhesive or cohesive in character.

The substrate used in the present investigation was a cellulose model—cellophane from which the glycerol plasticizer had been washed out. Adhesion of high polymers to cellulose is important in impregnation of tire cords, gluing of paper and board, production of fabric-based leather substitutes, etc. Cellophane is the most convenient of all the cellulose materials because of its mirror-smooth surface, so that it is possible to assume the area of nominal contact equal to the area of true contact, and to determine the character of the peeling visually.

The adhesives tested were several elastomers used in industry. The solvents used in applying the adhesives to the substrate were the solvents generally used in the production of rubber adhesives—gasoline, benzene, dichloroethane.

The joints were made and peeled apart under strictly standardized conditions<sup>6</sup>.

*Effect of the size of the macromolecules on adhesion.*—Table I contains our data on the force required to peal polyisobutylenes of different molecular weights from cellophane.

As Table I shows, the peeling resistance of polyisobutylene of molecular weight 7000 is practically zero, and the peeling is purely cohesive, i.e., it occurs in the layer of adhesive. With increase of molecular weight to 20,000 the

\* Reprinted from *Colloid Journal* 19, 279-284 (1957); an English translation by Consultants Bureau, Inc. of *Kolloidnyi Zhurnal* 19, 274-280 (1957).

resistance to separation increases sharply, and the separation is of the mixed type. Evidently in this case the cohesive strength of the adhesive is equal to the force required to peel the adhesive from the substrate. With molecular weights of 100,000 and over, the peeling is purely adhesive; the absolute value of the resistance to separation is the same in all cases, approximately 70 g/cm.

Table I also gives the results of experiments on the peeling from cellophane of polyisoprenes of molecular weight 20,000-150,000 (synthetic product) and 150,000-300,000 (natural rubber). Here again the polymer of lower molecular weight had considerably greater adhesion. The mixed type of separation of synthetic polyisoprene from cellophane shows that the cohesive strength of this polymer is approximately equal to the adhesive force.

At first sight it seems strange that natural rubber had such poor adhesion to cellophane. It is generally considered that natural rubber is an excellent adhesive. However, poor adhesion of natural rubber to cellophane has also been reported by others<sup>8</sup>.

TABLE I  
RESISTANCE TO SEPARATION OF CELLOPHANE AND POLYISOBUTYLENES  
OF DIFFERENT MOLECULAR WEIGHT

Adhesive	Molecular weight	Type of separation	Separation resistance in g/cm		
			Minim-	Maxi-	Average
Polyisobutylene	7,000	Cohesive	0	0	0
	20,000	Mixed	307	386	369
	100,000	Adhesive	61	70	67
	150,000	Adhesive	69	73	67
	200,000	Adhesive	60	71	68
Polyisoprene	20,000-150,000	Mixed	1112	1617	1379
	150,000-300,000	Adhesive	13	25	18

Table I shows that polymer adhesion increases with decreasing molecular weight. However, as the cohesive strength of a polymer decreases with decreasing molecular weight, the optimum gluing powers should probably be found in polymers of moderate molecular weight, which ensures adequate adhesion together with sufficient strength of the adhesive layer.

*Effect of the structure and shape of the macromolecules on adhesion.*—Table II gives data on the separation of various nonpolar or weakly polar polymers from cellophane.

Table II shows that adhesion of polybutadiene to cellophane is greater when the elastomer molecule has a more regular structure. Increase of the number of vinyl side chains in the molecule greatly diminishes adhesion. From the nature of the separation in this case it may be concluded that polymers with more regular structure have higher cohesive strength. This is in entire agreement with the modern views on the relationship between the mechanical properties and molecular structure of polymers. Styrene side chains in the butadiene polymer molecule have an analogous influence on adhesion.

A comparison of the adhesion of the copolymer containing 70% butadiene and 30% styrene, and of the copolymer containing 70% butadiene and 30% methylstyrene, to cellophane shows that adhesion is considerably lower in the latter case. This is probably to be attributed to the presence of a methyl group in the styrene residue.

The adverse effect of methyl groups in adhesion can also be seen from a comparison of the resistance of butyl rubber and polyisobutylene, of similar molec-

TABLE II  
RESISTANCE TO SEPARATION OF VARIOUS NONPOLAR OR WEAKLY POLAR ELASTOMERS FROM CELLOPHANE

Adhesives and their characteristics	Type of separation	Resistance to separation in g/cm		
		Minimum	Maximum	Average
Polybutadiene containing 50% butadiene groups in 1,4 position and 50% in 1,2 position	Adhesive	1433	1484	1445
Polybutadiene of the same molecular weight, containing 20% butadiene groups in the 1,4 position and 80% in the 1,2 position	Mixed	498	594	550
Copolymer containing 70% butadiene and 30% styrene	Cohesive	1153	1652	1368
Copolymer containing 50% butadiene and 50% styrene	Adhesive	3	22	14
Copolymer containing 70% butadiene and 30% methylstyrene	Mixed	274	1727	771
Butyl rubber, mol. wt. 60,000-80,000	Adhesive	272	307	298
Polyisobutylene, mol. wt. 80,000-100,000	Adhesive	61	70	67

ular weight, to separation from cellophane. The presence in the butyl rubber molecule of even a small number of isoprene groups, containing only one methyl group per four carbon atoms in the main chain, results in a sharp increase of adhesion. However, the increase of adhesion may also be the consequence of the presence of a small content of low molecular weight polymer fractions in the synthetic product.

The general conclusion to be drawn from the data in Table II is that the adhesion of a polymeric adhesive to cellophane decreases with increasing number of short side chains in the molecule.

*Effect of the presence of polar groups in the macromolecule on adhesion.*—The data in Table III show how the resistance to separation of cellophane from butadiene-acrylonitrile (NBR) copolymers varies with the contents of polar acrylonitrile groups.

Table III shows that the resistance to separation for NBR copolymers decreases with increasing contents of polar nitrile groups in the molecule. The type of separation also alters from cohesive to pure adhesive.

TABLE III  
RESISTANCE TO SEPARATION OF BUTADIENE-ACRYLONITRILE (NBR) COPOLYMERS OF DIFFERENT POLARITIES FROM CELLOPHANE

Adhesives and their characteristics	Type of separation	Resistance to separation in g/cm		
		Minimum	Maximum	Average
NBR copolymer containing 18.4% acrylonitrile groups	Cohesive	1380	1735	1638
NBR containing 28.6% acrylonitrile groups	Mixed	1144	1717	1382
NBR containing 37.7% acrylonitrile groups	Adhesive	125	138	132

## DISCUSSION OF RESULTS

Up to the present adhesion has been thought to be caused either by the action of molecular forces<sup>3,6</sup> or by formation of an electrical double layer at the interface<sup>7-9</sup>. However, as we have shown<sup>10</sup>, neither of these viewpoints is valid when both the adhesive and the substrate are high polymers.

In our theory, both adhesion of high polymers to each other and autohesion consists of diffusion of chain molecules or sections of them from one polymer into the other to form a stable bond constituting a gradual transition from one polymer to the other. It is quite obvious that the interdiffusion of two high polymers in contact is none other than mutual solution. Therefore adhesion of high polymers to each other is closely related to their mutual solubilities, which, as we have shown<sup>11</sup>, is largely determined by their polarity relationships.

If our diffusion theory of adhesion is correct, the adhesion of high polymers to each other should depend very largely on the ability of the macromolecules to diffuse into solids and on the mutual solubility of the high polymers. Unfortunately, almost nothing is known at the present time about these important characteristics of high polymers, and therefore verification of the views put forward above must be limited to finding the relationships between adhesion and molecular structure (molecular weight, form of the macromolecules, presence of polar groups) of the contacting polymers.

In our experiments the same substrate, cellophane, was used. Cellophane, like cellulose, consists of macromolecules containing polar hydroxyl groups. Because of the size and rigidity of these macromolecules, and the molecular forces acting between them, they are not capable of any appreciable diffusion into elastomers. Conversely, the molecules of the elastomers used in our investigations are fairly flexible and capable of diffusion. Therefore in our case it is sufficient to correlate the adhesion between cellophane and elastomers with the molecular structure of the latter.

*Effect of molecular size and shape of nonpolar elastomers on their adhesion to cellophane.*—We have seen that, with the same contact time, the adhesion of polyisobutylene to cellophane first decreases with increasing molecular weight, and then becomes practically constant. Experiments with polyisoprenes of different molecular weight do not contradict this result. The fact that adhesion ceases to be dependent on the molecular weight after the latter has reached a certain value has been reported by others for other materials<sup>4</sup>. In our theory, this can be explained in the same way as in the case of autohesion<sup>12</sup>: as the molecular weight increases, the number of free ends of molecules, capable of diffusing especially easily, diminishes. When the molecular weight is high, mainly chain segments diffuse, and their penetration into the spaces between the substrate molecules is difficult. Therefore a less stable bond will be formed in a given time between two high polymers in contact, and as the segment size does not depend on the length of the macromolecule, the adhesion ceases to depend on the molecular weight.

Another explanation of the fact that adhesion becomes independent of molecular weight above a certain value is the higher plasticity of the adhesives with lower molecular weight which, of course, favors diffusion. There are reports in the literature<sup>3</sup> that introduction of not too large amounts of plastizizers into high polymer adhesives improves adhesion. It is possible, of course, that the increase of adhesion with diminishing molecular weight is to be explained by the combined action of both these factors.

It should be noted here that the increase of adhesion with decreasing molec-

ular weight does not contradict the observed fact that bond strength increases with increasing molecular weight of the adhesive. The reason is that in most instances the joints are broken not at the adhesive-substrate boundary but within the adhesive layer. In such conditions the resistance to separation will, of course, increase with increasing molecular weight of the adhesive.

Thus, the question of the influence of molecular weight on adhesion needs to be reviewed in the light of the foregoing data. There are adequate grounds for believing that decrease of molecular weight, which decreases the cohesive strength of the substance, favors increased adhesion. This view is quite understandable from the viewpoint of the diffusion theory of adhesion—as the molecular size decreases the capacity of the molecule for diffusion increases, and adhesion should therefore increase also.

We have seen that determination of the adhesion of polybutadiene to cellophane showed that an increase of the number of butadiene groups in the 1,2 position in the adhesive molecule worsens the adhesion. The probable explanation is that, as the number of butadiene groups in the 1,2 position increases in the molecule, the ability of the molecule to diffuse becomes less on purely steric grounds (increased number of side groups).

Another example of the influence of side groups is provided by the adhesion of butadiene-styrene copolymers, with different proportions of the components, to cellophane. A small amount of styrene groups in the copolymer increases adhesion, but a large amount produces a decrease. Similar changes of adhesion with different proportions of the components in copolymer molecules have been observed by others<sup>4</sup>. The explanation again is that the copolymer molecules with a low styrene group content are largely regular in structure and therefore diffuse more easily into the substrate. A large number of styrene groups in the copolymer molecule decreases the ability to diffuse because of the presence of a large number of cumbersome side chains in the macromolecule and decreased chain flexibility.

As we have seen, replacement of styrene by methylstyrene groups in the copolymer molecule decreases adhesion. The probable reason for this is the considerable decrease of the diffusion capacity of the macromolecules owing to the presence of additional methyl groups. The results of experiments with polyisobutylene and butyl rubber lead to similar conclusions.

Reference was made earlier to the adverse effect of short side chains in the macromolecule on adhesion. However, if these side chains are long enough, they may act as individual chains which, for steric reasons, diffuse more readily into the substrate than do the middle regions of the molecular chains<sup>12</sup>. This is quite understandable, as the probability of entry of such a molecular end into a space between the substrate molecules is certainly higher than the probability of entry of a middle part of a molecule into the same space. This view is confirmed by the results of McLaren<sup>2</sup>, who showed that adhesion to cellophane increases in the polymethacrylate series from methyl methacrylate polymer to *n*-butyl methacrylate polymer. McLaren also showed that isopropyl and isobutyl methacrylate polymers have considerably lower adhesion to cellophane than the corresponding normal methacrylate polymers. This is in full agreement with our views on the influence of molecular shape on adhesion.

*Effect of polarity of the adhesive on adhesion to cellophane.*—First it must be pointed out that it is found experimentally that such nonpolar or weakly polar high polymers as polyisobutylene and polybutadiene have fairly high adhesion to polar cellophane. The reason, in our view, is the insufficiently close packing

of the cellulose molecules, owing to which the flexible and mobile molecules of the adhesive can diffuse into the cellulose. Another interpretation of the effect is that the hydrocarbon chains of the nonpolar adhesive are capable of dissolving in cellulose to a certain extent, thus forming a bond between the adhesive and substrate. Further, it has been found that butadiene-acrylonitrile copolymers have decreasing adhesion to cellophane with increasing contents of polar acrylonitrile groups in their molecules. Others<sup>2</sup> have also reported that high polymers containing nitrile groups in their molecules have poor adhesion to cellophane. Since cellophane molecules are strongly polar, this result seems at first sight incomprehensible—it would seem that the more strongly polar nitrile groups the polymer contains, the better would it dissolve in cellophane and the stronger would be the bond formed between the adhesive and the substrate. However, the contradiction is easily explained because, with increasing contents of polar groups in the macromolecules of the adhesive, the rigidity of the macromolecular chains increases and therefore their diffusion capacity diminishes. Moreover, adhesion decreases owing to the presence of often cumbersome polar side chains in the molecules, which hinder diffusion for steric reasons. Finally, the polar groups present in the polymer molecules may themselves interact by intermolecular forces, and this would also hinder diffusion.

Thus, the decrease of adhesion with increasing polarity of the adhesive in our experiments must be explained as a purely kinetic effect. It is important that if instead of the polar cellophane a nonpolar substrate was used, the adhesion would also decrease with increasing polarity of the adhesive. However, the interpretation of this effect would be different—in this case increase of the polarity of the adhesive would result in a decrease of the solubility of the adhesive in the substrate, i.e., it would be explained purely on thermodynamic grounds.

It should be noted that adhesion does not always diminish with increasing polarity of the high polymer. For example, McLaren<sup>3</sup> found that, with increasing chlorine content in chlorinated polyethylene, the adhesion of the polymer to cellophane first increases, then begins to decrease. McLaren also found that moderate contents of polar groups—chlorine, carboxyl, carbonyl, and hydroxyl—in the macromolecules may improve adhesion to cellophane. The possible explanation is that, for a moderately polar high polymer, the improvement of adhesion as the result of better solubility exceeds the decrease of adhesion caused by increased rigidity of the molecules and decreased diffusion of the polymer.

#### SUMMARY

1. The method developed by the authors has been used to study the influence of size, form, and polarity of macromolecules on the adhesion of high polymers to cellophane.
2. Adhesion of high polymers to cellophane increases with decreasing molecular weight. However, for maximum bond strength, the cohesive properties of the polymer must also be taken into account.
3. Increase of the number of short side chains in the polymer molecule lowers its adhesion.
4. The adhesion of a polymer to cellophane decreases with increasing contents of polar groups in its macromolecules.
5. The results are explained on the basis of the diffusion theory of high polymer adhesion developed by the authors.

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# INFRARED STUDY OF SOME STRUCTURAL CHANGES IN NATURAL RUBBER DURING VULCANIZATION \*

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## INTRODUCTION

In order to elucidate structural changes occurring during vulcanization, Sheppard and Sutherland<sup>1,2</sup> studied the infrared spectra, between 2 and 18  $\mu$ , of accelerated and unaccelerated sulfur vulcanizates. In the 6.0  $\mu$  region they found little evidence of changes in absorption due to double bonds. A band at 10.4  $\mu$  was attributed to *trans* hydrogens adjacent to a carbon-to-carbon double bond resulting from a shift of the double bond normally present in unvulcanized rubber. This band had been discovered earlier by Sears<sup>3</sup>. Salomon and Van der Schee<sup>4</sup> have confirmed, essentially, the findings of Sheppard and Sutherland<sup>1,2</sup>. The results of infrared studies of vulcanization through 1949 are summarized by Mann<sup>5</sup>.

The earlier studies had been made using single-beam instruments. The double-beam instruments now available are, of course, capable of greater definition in the critical double-bond region near 6.0  $\mu$  and in other regions where there occurs intense atmospheric absorption. For these reasons, some of the studies of these workers were repeated using a double-beam instrument. Since the work on accelerated and unaccelerated sulfur vulcanizates proved fruitful, additional studies were made of other vulcanization systems including those involving tetramethylthiuram disulfide (TMTD) alone, a peroxide, gamma rays, and sulfur dioxide and hydrogen sulfide (Peachey process).

Some spectra were also obtained in the region between 15 and 40  $\mu$  using a cesium bromide prism to determine the existence of bands in this region, which might be due to C—S and S—S linkages.

In order to support the work on sulfur vulcanization a study was made of the squalene-sulfur system, and chemical evidence was obtained for one of the infrared interpretations.

## EXPERIMENTAL PROCEDURE

Most of the infrared spectra were obtained with a Perkin-Elmer model 21 double-beam spectrophotometer equipped with a sodium chloride prism for the range between 2 and 15  $\mu$ , and a cesium bromide prism for the range between 15 and 40  $\mu$ . An attachment ordinarily used to hold small KBr disks was employed in most of this work. With this attachment, the specimen is inserted through the opening in the instrument cover to a position of minimum beam size, thus making possible the use of specimens as small as 0.375 in in diameter, which in some cases were all that could be obtained.

Additional measurements at higher resolution were made on certain bands

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using a Beckman IR-4 spectrophotometer equipped with two sodium chloride prisms. Some of the complete spectra were also obtained with this instrument.

Specimens of unvulcanized rubber were prepared by evaporating to dryness natural rubber latex which had been diluted with water sufficiently to give a film of satisfactory thickness. In addition, specimens of unvulcanized smoked sheet, crepe rubber, or purified rubber were prepared by hot-pressing the material between sheets of aluminum foil with the aid of a Carver press. It was found that a pressure of about 1000 to 4000 lb/in.<sup>2</sup> was sufficient to produce a specimen of suitable thickness, i.e., somewhere between 0.05 and 0.12 mm. The samples vulcanized by the Peachey process or by treatment with gamma rays were first pressed between sheets of aluminum foil for a short time at elevated temperature to obtain a thin sheet, and then subjected to the vulcanization treatment. All the other samples were vulcanized under pressure in a Carver press.

Compounding was done on a laboratory rubber mill equipped with rolls 3 in. by 8 in.

#### RESULTS

The results of this study are presented in typical spectra given in Figures 1 to 9, which are discussed in detail along with related spectra, in the sections that follow. The arrows in the figures indicate the pertinent bands in this study. The results are summarized in Table I. This table indicates changes in bands and in band intensities as a result of the various vulcanization processes, and is included for convenient reference in reading the discussions.

In this table and in the following discussions, it is to be emphasized that conclusions involving changes in band intensities are to be viewed with caution. In general, the intensities of absorptions in films, in addition to thickness, are influenced by factors such as scatter, inhomogeneity, surface reflection, and the effect of neighboring bands. These factors are important in rubber and especially so when the added solids used in vulcanization are present.

Consequently, in a number of cases it was not possible to come to a definite decision regarding changes in band intensities. However, in cases where a change in intensity appeared to occur, the change has been noted as a possible or apparent change, with the intention of indicating to the reader that the intensity change is at least a possible result of the treatment discussed.

*Unvulcanized natural rubber.*—Figure 1 shows the spectrum between 2 and 15  $\mu$  of a film of natural rubber obtained by the evaporation of water from latex. This spectrum is essentially the same as that obtained by previous investigators. Sheppard and Sutherland<sup>1</sup> suggest that the band at 3.05  $\mu$  may be due to the C—H stretching vibration of the "lone" hydrogen on the ethylene bond in rubber. If, on the other hand, this band is due to NH groups in proteins perhaps, or to OH groups, its position indicates that these groups are strongly hydrogen bonded. No interpretation of the weak absorption near 4.9  $\mu$  is possible beyond the fact that it occurs in the region where acetylenes, nitriles, isocyanates, allenes, and amino acids absorb; it is probably the same band that Sheppard and Sutherland<sup>1</sup> found at 4.98  $\mu$ . The bands near 5.75 and 5.85  $\mu$  may indicate two types of carbonyls; they may be due to carbonyls already present in the hydrocarbon chain, or formed by oxidation of the chain, or else to carbonyls in the resinous portion. They are probably the small bands near 5.8  $\mu$  mentioned by Dinsmore and Smith<sup>6</sup>, and Saunders and Smith<sup>7</sup>.

It is interesting to note that purification of natural rubber by the method of McPherson<sup>8</sup> does not change markedly the intensity of any of these bands.

TABLE I  
SPECTRAL RESULTS AND CONCLUSIONS<sup>a</sup>

Wavelength μ	Previous observa- tions <sup>b</sup>	P, Present; A, absent; I, increases; D, decreases; —, not investigated		Remarks					
		1 2 3 4 5 6 7 8 9	Unvulcanized Dried Coop- lated latex	Sulfur alone	Sulfur and ac- celer- ator com- binations	TMTD alone	Peachey oxide	Per- Gummis- ray <sup>c</sup>	
2.9	1.6	A	A	A	A	I	A	A	Probably oxidation band.
3.05	1.6,7	P	P	P	I	P	P	P	May increase in 3 than in 1 and 2. May increase in 5 with TMTD and BZ, and in 7, 8, and 9 (on 9, see text).
4.90	1 <sup>d</sup>	P	P	P	D	P	D	P	May increase in 5 with TMTD and in 6, 7, 8, and 9 (on 9, see text).
5.75	6.7 <sup>e</sup>	P	P	P	D	P	D	P	Either one or both characteristic of proteins or resins as such.
5.85	6.7 <sup>f</sup>	P	P	P	D	P	P	P	Possible decrease in 6.5 μ band. Possible decrease in 6.
6.02	1.6,7	P	P	P	D	P	P	P	Double bond in unvulcanized rubber.
6.10 { 6.10	6.7	P	P	P	P	P	P	P	Band at 6.02 μ unsharp in purified rubber; inflection in dried latex; shoulder in conjugated rubber; resolved at least to 6.02 μ band in vulcanizates containing more than 12 per cent sulfur (see text).
6.25	None <sup>g</sup>	A	A	P	D	A	A	A	Conjugated double bonds; band appears in sulfur vulcanizates with over 5 per cent sulfur.
6.5	1.6,7	A	A	P	P	A	I	I	Present in 5 with smaller quantity of TMTD; otherwise presence in 5 and 6 may be observed by bands in TMTD and BZ, may be increased in 7, 8, and 9 (on 9, see text).
10.4	1.2	A	A	P	P	A	A	A	Shifted double bond; confirmed for compounds containing more than 2 per cent sulfur; role of formation increased by accelerators.
11.95	1.2,6	P	P	D	D	P	P	P	Hydrogen on double bond in unvulcanized rubber.
14.3	{ None <sup>g</sup>	A	A	P	P	A	A	A	Appear in sulfur vulcanizates containing more than 12 per cent sulfur; sometimes present with accelerators (15% sulfur).
14.5	None <sup>g</sup>	A	A	P	P	A	A	A	Occur in sulfur vulcanizates with less than 12 per cent sulfur; usually present in 5 (15% sulfur) and in 6 (15% TMTD 4 hr and over at 125°C).
17.0	1.7,10 <sup>g</sup>	A	—	P	—	—	—	—	May be slight linearization of a shoulder on 17.5 μ band in unvulcanized rubber.
17.5	7,10	P	—	D	—	—	—	—	Band confirmed.
19.8	—	P	—	D	—	—	—	—	Band confirmed.
23.5	23.5	{ None <sup>g</sup>	P	—	A	—	—	—	Broad swelling centered near these wavelengths.
28.0	21.2	22.7	{ None <sup>g</sup>	A	—	P	—	—	These bands occur in region where S-S linkages absorb.
24.4	24.4	24.4	—	—	—	—	—	—	23.0

<sup>a</sup> Numbers indicate references in literature cited.

<sup>b</sup> Probably 4.38 μ band of Reference 1.  
<sup>c</sup> Probably one of weak bands near 5.8 μ in Reference 6 and 7.

<sup>d</sup> Newly observed.

<sup>e</sup> Probably band at 16.6 to 17.7 μ of Reference 1.

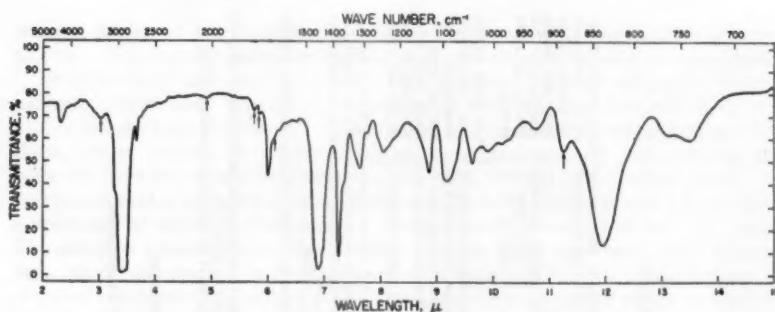


FIG. 1.—Infrared spectrum of film of dried natural rubber latex.

The purified rubber used here contained 98.7 per cent rubber hydrocarbon, 0.44 per cent protein, and 0.18 per cent ash. The sample also contained 1 per cent phenyl-2-naphthylamine added as an antioxidant, an amount that proved insufficient to affect the spectrum. This purified rubber had also been used by Roberts and Mandelkern<sup>9</sup> and was obtained from them. The fact that purification does not greatly reduce the intensity of these bands indicates that they are not related to the resin or protein content of the rubber, which is greatly reduced on purification, unless appreciable quantities of resin- or proteinlike units are in some way part of the polymer chain. Dinsmore and Smith<sup>12</sup>, and Saunders and Smith<sup>7</sup>, however, did not find the 3.05  $\mu$  band in deproteinized rubber. It should be pointed out that it is possible to explain all four of these bands as either combinations or overtones of frequencies observed for absorptions in Figures 1 and 2. These bands are of interest here since their intensities may be affected by certain vulcanization processes.

There is an inflection point at 6.1  $\mu$  in the spectrum of dried latex given in Figure 1. This absorption is all but absent in the spectrum of purified rubber, the only evidence of its presence being the unsymmetrical nature of the band at 6.0  $\mu$  which is broader on the longer wavelength side. On the other hand, this absorption appears as a strong shoulder in spectra of coagulated rubber,

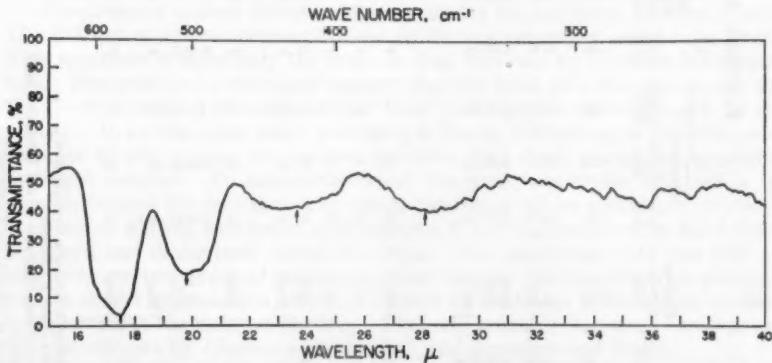


FIG. 2.—Far infrared spectrum of film of dried natural rubber latex.

i.e., Tensocrepe, pale crepe No. 1 thin, pale crepe No. 1 thick, smoked sheet and Tensosheet. Dinsmore and Smith<sup>6</sup> first attributed this shoulder to absorption by a terminal double bond. In a later article Saunders and Smith<sup>7</sup> concluded that the band at  $6.1\text{ }\mu$  was largely due to an impurity. The present work indicates that this impurity is probably introduced during coagulation. Apparently the strong shoulder at least is not, as suggested by Sheppard<sup>11</sup>, an overtone of the  $11.95\text{ }\mu$  band. It may be, however, that the residual absorption in purified rubber is due to terminal double bonds or to an overtone of the  $11.95\text{ }\mu$  band. The slight difference between dried latex and purified rubber, if real, may be due to an impurity in dried latex.

The coagulated samples also showed what is probably a somewhat stronger absorption at  $3.05$  and a band at  $6.5\text{ }\mu$ . Again, these effects are apparently due to impurities introduced during coagulation and not removed by the washing process.

As a result of a comparison of spectra of smoked sheet and purified rubber, Saunders and Smith<sup>7</sup> seem to consider not only the band at  $6.1$ , but also the bands at  $3.05$ ,  $5.75$ ,  $5.85$ , and  $6.5\text{ }\mu$  to be due largely to impurities.

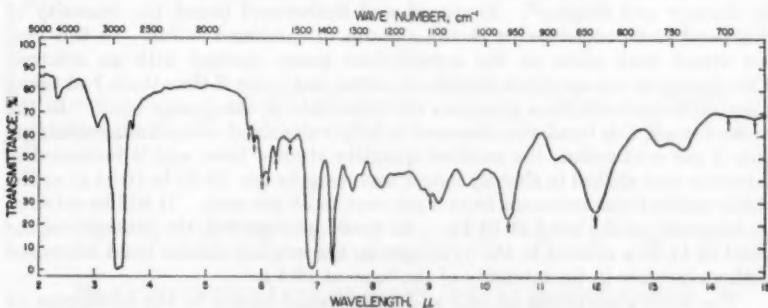


FIG. 3.—Infrared spectrum of natural rubber (pale crepe No. 1 thick) vulcanized with 15 per cent sulfur for 96 hr at  $125^\circ\text{ C}$ .

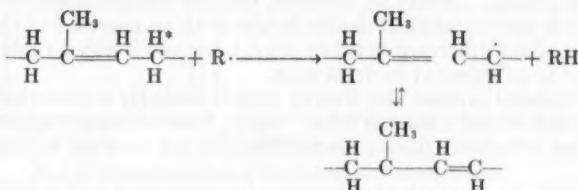
Figure 2 shows the spectrum of dried natural rubber latex in the region between  $15$  and  $40\text{ }\mu$ . The spectrum of purified rubber is essentially the same. There are two broad absorptions with peaks near  $17.5$  and  $19.8\text{ }\mu$ , respectively, in reasonable agreement with the findings of other workers<sup>7,10</sup>. It is probably the former to which Sheppard and Sutherland<sup>1</sup> refer as extending from  $16.6$  to  $17.7\text{ }\mu$ . In addition, there are two very broad swellings between  $21$  and  $30\text{ }\mu$  which have not been reported previously. The smaller bands beyond  $30\text{ }\mu$  are due to uncompensated atmospheric water-vapor absorption.

*Vulcanization with sulfur alone.*—In this work, some samples of natural rubber (pale crepe No. 1 thick) containing from  $2$  to  $25$  per cent sulfur and no zinc oxide were vulcanized approximately to completion (about  $20$  hr) at  $150^\circ\text{ C}$  while others containing  $15$  per cent sulfur and no zinc oxide were vulcanized for periods of time ranging from  $15$  min to  $4$  days at  $125^\circ\text{ C}$  and from  $1$  hr to  $20$  hr at  $150^\circ\text{ C}$ .

Figure 3 gives the spectrum between  $2$  and  $15\text{ }\mu$  of natural rubber vulcanized with  $15$  per cent sulfur for  $96$  hr at  $125^\circ\text{ C}$ . In addition to the changes indicated in Table I, some other unexplained changes near  $9.0\text{ }\mu$  have taken place during vulcanization. These changes become noticeable with about  $5$  to  $8$

per cent sulfur; they also occur in accelerated vulcanizates, but not in the other types of vulcanizates discussed here.

The band at  $10.4 \mu$  not present in unvulcanized rubber has been interpreted by Sheppard and Sutherland<sup>2</sup> to be due to the out-of-plane deformation vibration of the *trans* hydrogens on a double bond resulting from a shift of the following type:



where  $\text{R}\cdot$  is a free radical. These workers pointed out that this is consistent with the idea of  $\alpha$ -methylene initiation of the sulfuration reaction as advanced by Farmer and Shipley<sup>12</sup>. Sheppard and Sutherland found the intensity of this band to be correlated with the amount of combined sulfur. In this case the attack took place on the  $\alpha$ -methylene group marked with an asterisk. This change in the spectrum would, of course, not occur if the attack had taken place on the  $\alpha$ -methylene group on the other side of the double bond. In the present work, this band was observed in fully vulcanized compounds containing only 2 per cent sulfur, the smallest quantity studied here, and it increased in intensity and shifted to slightly longer wavelengths (ca.  $10.35$  to  $10.44 \mu$ ) as the sulfur content was increased from 2 per cent to 25 per cent. It will be referred to, however, as the band at  $10.4 \mu$ . As would be expected, the intensity of the band at  $11.95 \mu$  related to the hydrogen on the original double bond decreased with an increase in the intensity of the band at  $10.4 \mu$ .

The weak absorptions at  $14.3$  and  $14.8 \mu$  could be due to the hydrogens on the corresponding *cis* configuration. It is reasonable to expect both isomers to be formed during the double-bond shift. These bands could also be caused, however, by C—S linkages, or by skeletal vibrations not characteristic of any particular functional group. These bands appear as separate absorptions in fully vulcanized compounds containing more than 12 per cent sulfur. With sulfur concentrations from 2 to 12 per cent, only a broad general absorption appears that is centered near  $14.5 \mu$ . The newly discovered sharp band at  $6.25 \mu$  occurs in the region where conjugated double bonds absorb, and is treated separately in a later section. It occurs in all rubber-sulfur vulcanizates containing 5 per cent or more of sulfur, and its intensity increases with increasing sulfur content.

The weak broad band near  $6.5 \mu$  is presumably the same band reported by Sheppard and Sutherland<sup>1</sup> as occurring at  $6.52 \mu$  in unvulcanized rubber mixes to which stearic acid and zinc oxide had been added. They attributed this band to the stearate ion and reported that it disappeared on vulcanization. However, Ellis and Pyszora<sup>13</sup> have shown that the intensity of the band increases again to approximately its original value when the specimen is allowed to remain at room temperature for 18 hr. They attribute the observed effects to an interaction between natural rubber and zinc stearate that is not related to the vulcanization process. The compound used to obtain Figure 3 did not contain added zinc oxide or stearic acid, but the original rubber sample

showed an absorption at  $6.5 \mu$  which, as suggested earlier, may result from impurities introduced during coagulation. The intensity of this band sometimes appeared to be reduced on vulcanization in this work.

The presence of zinc oxide in sulfur vulcanizates of Tensocrepe or pale crepe No. 1 thin, leads to no apparent change in the rate of the double-bond shift and the band at  $6.25 \mu$  appears about as soon as it does without zinc oxide. There usually seems to be some reduction in the intensity of either or both the carbonyl bands near  $5.75$  and  $5.85 \mu$ .

There is a change in the relative intensities of the bands at  $6.0$  and  $6.1 \mu$  as a result of vulcanization. The increase of the  $6.1 \mu$  band relative to the band at  $6.0 \mu$  is noticeable in compounds containing 12 per cent sulfur, and increases with increased sulfur content until with 25 per cent sulfur it becomes the more prominent band, while the band at  $6.0 \mu$  appears only as a shoulder.

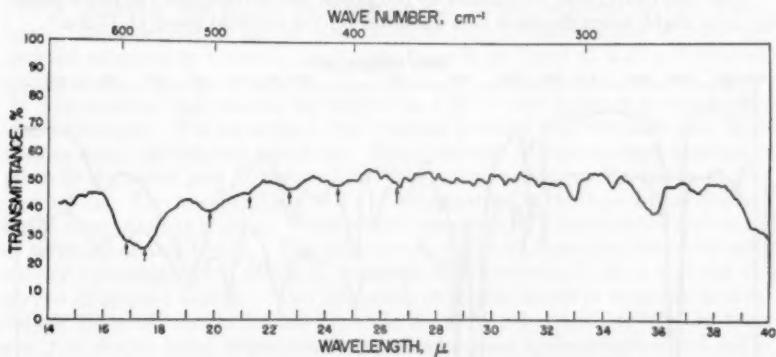


FIG. 4.—Far infrared spectrum of natural rubber (pale crepe No. 1 thick) vulcanized with 13 per cent sulfur for 20 hr at  $150^\circ \text{C}$ .

Under higher resolution, the band at  $6.1 \mu$  in vulcanized rubber may be resolved into two components at  $6.10$  and  $6.13 \mu$  with the main "6  $\mu$ " band appearing at  $6.02 \mu$ . The shoulder at  $6.1 \mu$  in unvulcanized rubber could also be due to two components, but this fact is not quite as apparent as in the case of vulcanized rubber.

At present it cannot be said with certainty whether there is an actual increase in the intensity of the  $6.1 \mu$  band on vulcanization or whether the observed relative change is due entirely to a decrease in the  $6.0 \mu$  band.

Because of the uncertainty of the nature of the band at  $6.1 \mu$ , and because the absorptivity of double-bond stretching vibrations is quite variable, no quantitative statement can be made about changes in unsaturation during vulcanization except that in accordance with the results of previous workers<sup>1,2,4</sup> even with 25 per cent sulfur considerable unsaturation of various types including those absorbing at  $6.1 \mu$  remains. To this residual unsaturation should now be added that due to the conjugated double bonds absorbing at  $6.25 \mu$ .

The same structural changes take place when natural rubber is vulcanized at  $150^\circ \text{C}$  but at an accelerated rate. There is often some increase in carbonyl structure, which also results from heating rubber alone at this temperature.

It is interesting to note that in a spectrum of a vulcanizate of Coral rubber, a synthetic polyisoprene<sup>14</sup>, the intensities of the band at  $6.25 \mu$  indicating con-

jugation and the band near  $6.1 \mu$  were considerably greater relative to the band at  $6.0 \mu$  than in the case of vulcanized natural rubber with the same amount of added sulfur (15%). The band at  $6.0 \mu$  was reduced to a slight shoulder on the band at  $6.1 \mu$ . The spectrum of the unvulcanized Coral rubber used here contained small bands near  $6.1, 6.2, 6.3$ , and  $6.65 \mu$ .

Figure 4 shows the spectrum between 15 and  $40 \mu$  of natural rubber (pale crepe No. 1 thick) vulcanized with 13 per cent sulfur for 20 hr at  $150^\circ C$ . It will be noted that: (1) There is some reduction in the intensity of the band at  $17.5 \mu$ , (2) the broad band at  $19.8 \mu$  is reduced, (3) the two consecutive swellings in the region between  $21$  and  $30 \mu$  have disappeared, and (4) these swellings have been replaced by weak bands at  $21.2, 22.7, 24.4$ , and  $26.6 \mu$ . No interpretation of these bands is possible at the present time beyond the observation that S—S linkages absorb in this region.

The band at  $17.0 \mu$ , mentioned by Sheppard and Sutherland<sup>1</sup>, appears possibly as a slight intensification of a shoulder on the original band at  $17.5 \mu$ .

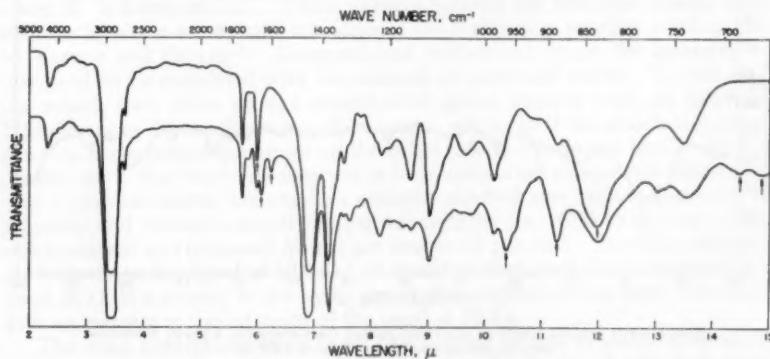
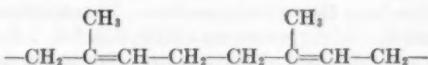


FIG. 5.—Infrared spectra of squalene and squalene-sulfur reaction product. Upper curve: Eastman practical grade (90%) squalene. Lower curve: Eastman (90%) squalene after reaction with 15 per cent sulfur for 22.5 hr at  $150^\circ C$  under nitrogen.

Gehman<sup>15</sup>, and Gehman and Osterhoff<sup>16</sup> have obtained Raman spectra of portions of acetone-extracted rubber soluble in petroleum ether or ethyl ether. Apparently, reported attempts to obtain Raman spectra of whole rubber have been unsuccessful because of difficulties due to Rayleigh scattering by rubber and by particles in the rubber as well as fluorescence of the nonrubber constituents of the whole sample. Attempts at the Bureau to obtain Raman spectra of whole rubber both unvulcanized and vulcanized have also been unsuccessful for the same reason. Raman spectra of vulcanized rubber, if obtained, would shed light on the existence of C—S and S—S linkages, which are generally known to produce stronger effects in the Raman spectrum than in the infrared, and should aid in establishing the identity of some of the infrared bands observed in this work.

*Reaction between squalene and sulfur.*—Squalene (a hexaisoprene), having a lower molecular weight and being a liquid, is more useful for certain experiments than rubber. It has been suggested by Bloomfield<sup>17</sup> that squalene, because of its molecular complexity, is more similar to long chain polyisoprenes than smaller compounds that have been used as rubber substitutes. It should be well adapted for the study of the structural changes of the double-bond shift

and conjugation discussed here. If we consider two adjacent isoprene units in the squalene molecule



it will be seen that a conjugated system could appear as a result of either a shift of two double bonds toward each other or two successive shifts of one double bond. It could also result from the introduction of a new double bond between two original double bonds. Similar possibilities for conjugation of this type, of course, exist in natural rubber. The spectrum of Eastman practical grade (90%) squalene given in the upper part of Figure 5 is essentially the same as that obtained by other workers<sup>18-21</sup>. It is similar in many respects to that of rubber as shown in Figure 1, including the band at  $6.0\text{ }\mu$  and the strong absorption at  $12.0\text{ }\mu$ , probably due to the hydrogen on the carbon adjacent to the double bond. Furthermore, it has no absorption at  $10.4\text{ }\mu$  characteristic of *trans* hydrogens adjacent to a double bond, and there is no band at  $6.25\text{ }\mu$  indicating conjugation.

This material was reacted for 22.5 hr at  $150^\circ\text{ C}$  with sulfur in a sealed tube under nitrogen. The squalene sulfur reaction product was very dark and more viscous than the original squalene. The spectrum of the reaction product is given in the lower part of Figure 5. This spectrum contains the bands at  $10.4$  and  $6.25\text{ }\mu$ . The new band near  $6.1\text{ }\mu$  is accompanied in this case by an increase in the absorption at  $11.25\text{ }\mu$ . Both effects have been<sup>6,22</sup> related to the formation of terminal double bonds. This situation is different from that observed with rubber vulcanizates for which an increased absorption at  $11.25\text{ }\mu$  was not observed (Figures 1 and 3). The migration of double bonds in squalene as a result of different treatments has been discussed by other authors<sup>18,20</sup>. In their study of double bond migrations in squalene during hydrogenation and dehydrogenation, Dale and Artun<sup>18</sup> found evidence of conjugation in the ultraviolet spectrum but no band at  $6.25\text{ }\mu$  in the infrared spectrum. There are also two bands near  $14.5$  and  $14.9\text{ }\mu$  which are reasonably close to the bands at  $14.3$  and  $14.8\text{ }\mu$  which in sulfur vulcanizates were attributed to the C—S linkage, to hydrogens *cis* to a double bond, or to skeletal vibrations.

*Chemical evidence of conjugated double bonds.*—Farmer and Shipley<sup>12</sup> have discussed the possibility of conjugated systems in vulcanization. Other authors<sup>23-26</sup> have mentioned apparently conjugated reaction products formed in the study of vulcanization using small molecules.

The band observed in these studies at  $6.25\text{ }\mu$ , if not due to conjugation, could be the result of combinations or overtones of absorptions occurring at other frequencies. None of the bands or combinations of bands observed to increase on vulcanization could account for the  $6.25\text{ }\mu$  band in this manner. However, in view of the apparent importance of this band, which is discussed later, it was deemed desirable to attempt to verify the presence of conjugated systems by chemical means. This was accomplished by demonstrating that a reaction takes place between the squalene-sulfur reaction product and maleic anhydride and that, as a result of this reaction, the band at  $6.25\text{ }\mu$  is removed.

Compounds containing conjugated double bonds normally react with maleic anhydride to form adducts in which the conjugation is removed not only from the compound in question but also from the anhydride. Examples of this Diels-Alder type of reaction are described by Klotzel<sup>27</sup>.

A portion of the squalene-sulfur reaction product (0.17 g) was mixed with

0.04 g of maleic anhydride, Fisher reagent. The mixture was agitated and heated for about 15 min to produce good mixing and a spectrum was obtained using a heated cell to keep the mixture molten. This spectrum is given in the upper half of Figure 6. Absorptions near 5.05, 5.2, 5.4, 5.6, 7.8, 7.9, 8.1, 9.5, 11.25, 11.55, 11.9, and 14.35 are at least in part due to the presence of maleic anhydride. It will also be noted that the bands near 6.0 and 6.1 due to the squalene-sulfur reaction product are quite apparent. The broadening of the band at  $6.25 \mu$  is probably due to the absorption of the maleic anhydride that occurs at  $6.27 \mu$ . Though there is no evidence of complete removal of conjugation, the extension of the band at  $10.4 \mu$  to  $10.55 \mu$  indicates that some reaction has already taken place.

This mixture was then reacted for 70 hr at  $100^\circ \text{C}$  in a sealed tube under nitrogen. The tube was cooled, broken open, and the reaction mixture heated until completely melted. After mixing with a spatula, a spectrum was obtained in a heated cell to maintain the liquid state of the sample.

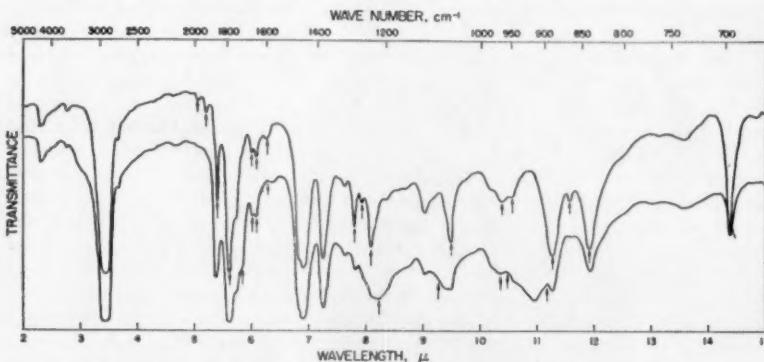


FIG. 6.—Infrared spectra of squalene-sulfur reaction product and maleic anhydride. Upper curve: mixture of 0.17 g squalene-sulfur reaction product and 0.04 g maleic anhydride before reaction. Lower curve: above mixture after reaction for 70 hr at  $100^\circ \text{C}$  in a sealed tube under nitrogen.

The spectrum of the final reaction mixture is given in the lower part of Figure 6. Increased absorption near  $5.8 \mu$  and just beyond  $8.0$  and  $9.0 \mu$  as well as the greatly increased absorption from about  $10.5$  to beyond  $11.0 \mu$  indicate that reaction has taken place. The continued absorption at  $6.0$  and  $6.1 \mu$  indicates that at least a portion of this part of the squalene-sulfur reaction product is still intact. It will be noticed that the band at  $6.25 \mu$  has been removed completely, leaving, in fact, a slightly increased transmittance. The fact that a reaction has taken place and the band at  $6.25 \mu$  has been removed is evidence of the presence of conjugated double bonds in the original reaction product. It is interesting to note that there is still absorption at  $10.4 \mu$  probably due in part, at least, to shifted double bonds which are not conjugated. This, of course, assumes that the double bond in the final reaction product is *cis* as in the case of the reaction product obtained with butadiene and maleic anhydride<sup>27,28</sup>.

A sample of unreacted squalene mixed with maleic anhydride and run as a control showed no change after heating, except for the production of a band at  $10.9 \mu$  and shoulders at  $5.35$  and  $5.85 \mu$  indicating that the other changes ob-

served with the squalene-sulfur reaction product are probably due to the Diels-Adler type of reaction. The quantity of maleic anhydride used in the above experiment was sufficient to react completely with one conjugated system per squalene molecule. Doubling this quantity of anhydride led to the same spectral picture, but increasing it fivefold obscured all the bands of the squalene-sulfur reaction product.

Preliminary work had shown that the reaction between maleic anhydride and the squalene-sulfur reaction product does not take place in 8 days at room temperature. Backer and Blaas<sup>29</sup> have used temperatures between 150° and 165° C in reactions involving thioether compounds containing conjugated double bonds, molecular types which might be present in the squalene-sulfur reaction product. These higher temperatures were avoided here in an attempt to eliminate the non-Diels-Adler type reactions involving maleic anhydride and various hydrocarbons<sup>28</sup>.

It is interesting to note that, since maleic anhydride does not react with the benzene nucleus, the conjugated systems in the squalene-sulfur reaction product are not phenyl rings. This conclusion is consistent with the spectrum in the lower half of Figure 5 which shows no change in the 11 to 15  $\mu$  region where various aromatic compounds absorb. Similarly, this lack of new bands in the 11 to 15  $\mu$  range in the spectrum of vulcanized rubber indicates that the conjugation in vulcanized rubber is probably not caused by phenyl rings which might result from reversion during the vulcanization process.

Using purified squalene available only in small quantities, spectra were obtained on squalene and the squalene-sulfur reaction product in order to determine the effect of the impurities present in the practical grade. Except for the absence of carbonyl groups in the purified material, the spectra of the unreacted and reacted samples were qualitatively similar. Reaction of maleic anhydride with squalene-sulfur reaction product obtained from purified squalene also resulted in removal of the band at 6.25  $\mu$ . There was, however, a sharper band at 5.8  $\mu$ , and differences in the absorption pattern between 9 and 11  $\mu$ . These differences are not unexpected in view of the purified nature of the sample.

Following the work with squalene, attempts were made to remove the band at 6.25  $\mu$  in rubber-sulfur vulcanizates by adding various dienophiles to the compound before vulcanization. Of the reagents tried, maleic anhydride, diethyl fumarate, di(2-ethylhexyl) maleate and dicetyl maleate, only diethyl fumarate produced an apparent decrease in the intensity of the band at 6.25  $\mu$ . The larger quantity (13.5%) produced a greater apparent effect than the smaller quantity (5%), but did not completely remove the band.

*Vulcanization with sulfur and accelerators.*—In order to determine the effect of accelerators on some of the structures found in unaccelerated samples, spectra were obtained on the vulcanizates of pale crepe rubber given in Table II. The quantities of sulfur and accelerator used in these studies were much larger than those used in conventional compounds in order to produce pronounced effects in the infrared spectra. Compounds A through E were vulcanized at 125° C for periods of time up to 48 hr. Compound F was vulcanized for from 7.5 min to 8 hr at 150° C.

In samples accelerated with TMTD and BZ (compounds A through E) the rate of the double-bond shift was greater than in the unaccelerated samples. For example, about as much double-bond shift occurred in 2 hr in samples accelerated with BZ as occurred in 16 hr with samples accelerated with the larger quantity of TMTD. This same amount of double-bond shift occurs in about

48 to 70 hr in unaccelerated samples. The effect of the smaller quantity of TMTD on the double-bond shift may not have been as great as that of the larger quantity.

In comparison with unaccelerated compounds, however, conjugation, as determined by the presence of a band at  $6.25 \mu$ , was either virtually eliminated or its first appearance was delayed relative to a given amount of double-bond shift. Moreover, once slight conjugation had appeared, further vulcanization of these accelerated compounds did not cause as great an increase in the amount of conjugation as was observed in unaccelerated compounds.

In all cases the relative change in the intensities of the bands at 6.0 and  $6.1 \mu$  was observed as was in all but the shorter cures, a band or bands between 14 and  $15 \mu$ . The band at  $6.5 \mu$  was present in samples containing the smaller quantity of TMTD only; in the other samples it was probably partly obscured by bands from TMTD and BZ.

TABLE II  
ACCELERATED COMPOUNDS

Constituent	Amount in compound					
	A %	B %	C %	D %	E %	F %
Pale crepe No. 1 thin	83	77	77	—	—	77
Tensocrepe	—	—	—	77.5	77.5	—
Sulfur	15	15	15	15	15	15
Tetramethylthiuram disulfide (TMTD)	1.5	7.5	—	7.5	—	—
Zinc dibutyl dithiocarbamate (BZ)	—	—	7.5	—	7.5	—
Mercaptobenzothiazole (MBT)	—	—	—	—	—	7.5
Zinc oxide	0.5	0.5	0.5	—	—	0.5

In samples accelerated with mercaptobenzothiazole (MBT) the rate of the double-bond shift was again more rapid than without the accelerator but nothing could be determined regarding the presence of conjugation since the benzene nucleus in the accelerator also has an absorption at  $6.25 \mu$ .

In some of the samples accelerated with TMTD and BZ, there may be an intensification of the band at  $3.05 \mu$ . There may also be an increase in the intensity of the small band at  $4.9 \mu$  in a few of the samples accelerated with TMTD. Accelerators also seem to reduce either or both of the carbonyl bands near  $5.75$  and  $5.85 \mu$ .

*Vulcanization with TMTD.*—Compounds of pale crepe No. 1 thin containing 15 per cent TMTD and 0.5 per cent ZnO alone were vulcanized at  $125^\circ$  and  $150^\circ$  C for periods of time varying from 7.5 min to 40 hr at the lower and 8 hr at the higher temperature. A spectrum of a sample vulcanized for 2 hr at  $125^\circ$  C is typical and is given in Figure 7. Unlike spectra of compounds in which TMTD serves as an accelerator in sulfur vulcanization, this spectrum shows no evidence of either conjugation or the double-bond shift indicated by bands at  $6.25$  and  $10.4 \mu$ , respectively. There is, however, an absorption near  $10.3 \mu$ . There also seems to be no appreciable change in the absorptions at  $12.0$  and near  $6 \mu$  as a result of different periods of vulcanization, indicating that the double bond in the polymer is not noticeably affected.

After curing there is sometimes an apparent increase in the intensity of the weak band observed at  $4.9 \mu$ . As curing proceeds, there is a decrease in ab-

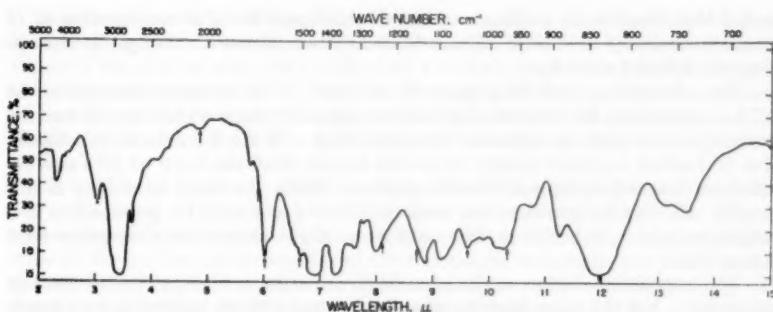


FIG. 7.—Infrared spectrum of natural rubber (pale crepe No. 1 thin) vulcanized with 15 per cent tetra methylthiuram disulfide (TMTD) and 0.5 per cent zinc oxide for 2 hr at 125° C.

sorptions at 6.65, 8.1, 8.7, 9.6, and 10.3  $\mu$ , wavelengths at which TMTD itself absorbs. This indicates destruction of the TMTD during the curing process. The band at 5.85 attributed to carbonyl absorption in rubber seems to be reduced. The band at 14.5  $\mu$  appears in samples vulcanized over 4 hr. Again, the band at 6.5  $\mu$  may be obscured by a band in TMTD.

In some samples vulcanized for the longer periods of time, there is increased absorption near 10.4  $\mu$  which disappears after the sample has been allowed to stand in air at room temperature.

*Vulcanization by the Peachey process.*—In preparing samples for this type of vulcanization, one piece of aluminum was stripped off the pressed sample leaving the rubber film on the other piece of aluminum. The rubber film (pale crepe) on the aluminum was cut into small strips and these strips were attached to a wire rack in a tube and vulcanized by the Peachey process for from 1 to 24 cycles as described in the paper by Bekkedahl, Quinn, and Zimmerman<sup>20</sup>. A single cycle consisted of passing sulfur dioxide over the sample for 5 min, followed by a brisk 10-sec sweep of air to remove the sulfur dioxide gas not adsorbed by the samples, and then passing hydrogen sulfide over the sample for 5 min, followed by another brisk 10-sec sweep of air.

Spectra were obtained on a number of these samples, of which the one given in Figure 8 for the sample receiving an 8-cycle treatment is typical. It will be

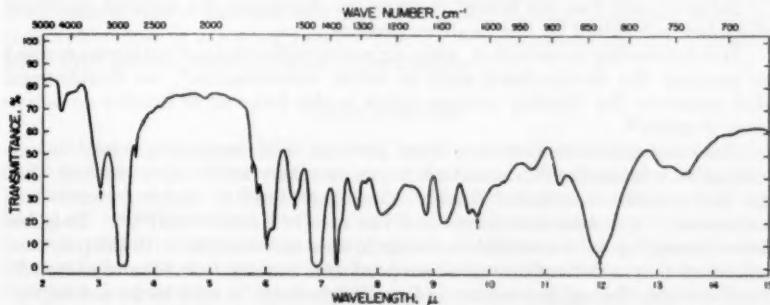


FIG. 8.—Infrared spectrum of natural rubber (pale crepe) vulcanized with sulfur dioxide and hydrogen sulfide (Peachey process) using 8 cycles of both gases.

noted that there is no evidence of the double-bond shift, of conjugation or of bands between 14 and 15  $\mu$ . There is also little evidence of changes in absorption at 12.0 and near 6  $\mu$ .

The absorption at 3.05  $\mu$  appears stronger. The carbonyl absorption at 5.75  $\mu$  appears to be reduced, and the strong absorption at 6.5 due to ionized carboxyl or to nitro groups may be intensified. If the 6.5  $\mu$  band is actually due to ionized carboxyl groups, it would appear that the band at 5.75  $\mu$  is related to the carboxylic acids in the rubber. Since the band at 5.75  $\mu$  is not greatly affected by purification, some of these acids may be attached to the polymer chain. In addition, there are some slight changes in absorption near 9.8  $\mu$ .

The intensities of these various bands do not seem to change much from 2 to 24 cycles. For the more highly vulcanized samples there seemed to be a tendency for the other carbonyl absorption at 5.84  $\mu$  to be reduced. At 24 cycles there was some slight evidence of a band at 10.4  $\mu$ . However, the more highly vulcanized samples had thickened during the process and comparison of their

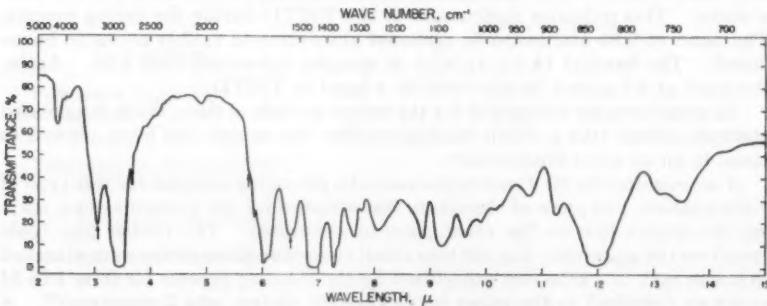


FIG. 9.—Infrared spectrum of natural rubber (pale crepe) vulcanized with 4.0 per cent di-tertiary butyl peroxide for 2.5 hr at 135° C.

spectra with others was rather difficult. It should be noted that only two cycles are required for an optimum cure and that a sample treated with 25 cycles might be expected to contain nearly 9.0 per cent combined sulfur, while one treated with only 8 cycles might contain somewhat over 7 per cent combined sulfur<sup>30</sup>.

Salomon and Van der Schee<sup>4</sup> observed no changes in the infrared spectrum of rubber vulcanized by the Peachey process.

It is interesting to note that, while an active sulfur radical has been assumed to produce the double-bond shift in sulfur vulcanization<sup>31</sup>, no double-bond shift occurs in the Peachey process which is also believed to involve an active form of sulfur<sup>32</sup>.

*Vulcanization with di-tertiary butyl peroxide.*—In comparing peroxide vulcanization with sulfur vulcanization it was necessary to choose a peroxide that did not contain conjugated double bonds. Di-tertiary butyl peroxide was satisfactory from this standpoint and has received some study<sup>33,34</sup>. It is believed to act by a free radical mechanism, does not combine with the polymer, and forms only volatile decomposition products, tertiary-butanol and acetone<sup>34</sup>. Furthermore, the oxygen content of the vulcanizate is said to be not significantly higher than that of the raw rubber<sup>34</sup>.

Samples of pale crepe natural rubber were prepared containing 1.5, 4.0, and

7.25 per cent peroxide. These samples were vulcanized for different periods of time varying from 15 min to 24 hr at 125° and 135° C. The spectrum given in Figure 9 was typical and was obtained on a sample containing 4.0 per cent peroxide vulcanized for 2.5 hr at 135° C. The apparent changes have been noted in Peachey vulcanization. There is a possible increase in the intensities of the bands at 3.05 and 6.5  $\mu$ , and a possible reduction in the carbonyl absorption at 5.75  $\mu$ .

It was found, however, that these apparent changes were present in a sample (containing 7.25% peroxide) which had not been vulcanized, i.e., heated above the temperature involved in milling. However, this sample exhibited none of the mechanical properties of the vulcanized materials, nor was it transparent and free from tackiness. Different times of vulcanization for the samples containing the different quantities of peroxide did not change the spectrum appreciably. Slight increases in absorption at 8.4 and 10.3  $\mu$  were noted when samples containing 7.25 per cent peroxide were vulcanized for 24 hr at 135° C. Only a very slight change was noted at 8.4  $\mu$  and none at 10.3  $\mu$  when these samples were vulcanized for 24 hr at 125° C.

*Vulcanization with gamma rays.*—In order to compare the structural changes observed for sulfur vulcanization with those resulting from gamma rays, pressed films of pale crepe rubber alone and with 8 and 15 per cent sulfur were exposed to a gamma-ray source of 50 curies strength for 120 hr (exposure dose of  $10^6$  to  $10^7$  roentgens) in air and under a vacuum. This exposure is sufficient to cause gelation. The treated specimens were quite sticky and some of them became too thick to give satisfactory spectra.

The changes occurring in the sample containing no sulfur when irradiated in air appear to be the same as those resulting from compounding with peroxide as indicated in Figure 9. For the specimens containing no sulfur and vulcanized in a vacuum and for the samples containing 8 and 15 per cent sulfur vulcanized either in air or in a vacuum, the spectra were not sufficiently satisfactory to estimate the status of the bands at 3.05 and 6.5  $\mu$ ; however, the band at 5.75  $\mu$  did not seem to be reduced. None of the specimens showed any evidence of conjugation. Because of an incomplete spectrum, the status of the band at 10.4  $\mu$  could not be determined for the specimen containing no sulfur and vulcanized in a vacuum, but in all other cases there was no evidence of a double-bond shift.

Sears and Parkinson<sup>35</sup> and Sears, Parkinson, Sisman, and Towns<sup>36</sup> have exposed Hevea presumably vulcanized and containing sulfur, zinc oxide, stearic acid, benzothiazolyl disulfide, and phenyl-2-naphthylamine to gamma radiation (absorption dose of  $2.2 \times 10^9$  rads). They report a continuation of the double-bond shift already started during vulcanization.

### CONCLUSIONS

Infrared studies have been made of natural rubber vulcanized with sulfur alone and also with sulfur and various accelerators. The spectral change (appearance of band at 10.4  $\mu$ ) resulting from the double-bond shift observed by Sheppard and Sutherland<sup>2</sup> was verified for compounds containing 2 per cent or more of sulfur. The presence of conjugated double bonds in compounds containing 5 per cent or more of sulfur has been indicated spectroscopically for the first time (appearance of band at 6.25  $\mu$ ) and supported by chemical evidence obtained from studies performed with squalene-sulfur reaction product and maleic anhydride. Conjugation presumably results from either two double-

bond shifts, or the introduction of a new double bond. Sheppard and Sutherland<sup>2</sup> have shown the double-bond shift to be correlated with the amount of combined sulfur.

In general, the effect of such accelerators as zinc dibutyl dithiocarbamate (BZ) and tetramethylthiuram disulfide (TMTD) is to reduce at least the amount of conjugation occurring with a given amount of double-bond shift and hence with a given amount of combined sulfur. Apparently these accelerators either prevent the formation of the conjugated double bonds or react to remove them after they are formed. Accelerated compounds also show evidence of reduced absorption due to carbonyl groups and possible increased absorption due to OH groups as the most likely structures.

Compounds cured with TMTD alone, peroxides, gamma rays, or sulfur dioxide and hydrogen sulfide (Peachey process) do not show evidence of the double-bond shift or of conjugation. They do show a possible decrease in carbonyl structures, and in the case of the last three, possible increased absorption due to OH and ionized carboxyl groups. Again, the structures named seem to be the most likely ones involved.

Apparently, the double-bond shift and the resulting conjugation are primarily phenomena related to the use of elemental sulfur. The other vulcanization systems studied evidently involve different mechanisms.

There is, during sulfur vulcanization, an increase in the intensity of the band near  $6.1\text{ }\mu$  relative to that of the band at  $6.0\text{ }\mu$ . This change in relative intensity is noticeable with 12 per cent sulfur and increases with increased sulfur content. In rubber-sulfur vulcanizates, at least, the band near  $6.1\text{ }\mu$  has been resolved into a doublet with one absorption at  $6.10\text{ }\mu$  and the other at  $6.13\text{ }\mu$ .

The fact that the double-bond shift, conjugation, etc., were observed spectroscopically in this work only with certain minimum quantities of sulfur or times of vulcanization, does not imply that they do not actually occur with less sulfur or shorter times of vulcanization. It is only reasonable to assume that they are a continuing part of the overall vulcanization reaction and that the condition of occurrence of the bands results from their absorptivity and the particular method of spectroscopic study employed.

It is well-known that rubber-sulfur compounds, accelerated compounds, and compounds cured with TMTD alone (all containing the usual percentages of compounding ingredients) are increasingly resistant to aging in the order named. If the present studies can indeed be extrapolated to the smaller percentages of compounding ingredients usually employed, the concentration of conjugated double bonds should also decrease in the same order. Since conjugated double bonds are known to be highly reactive, it is reasonable to assume that there should be some relationship between the ease of oxidation and the concentration of conjugated double bonds in the compound.

Preliminary observations have revealed that, as a sulfur-vulcanized film of rubber oxidizes, the appearance of absorption bands of  $\text{C}=\text{O}$ ,  $\text{C}-\text{O}$ , and OH groups in the infrared spectrum is accompanied, among other things, by a reduction in the conjugated double-bond absorption at  $6.25\text{ }\mu$ .

It should be noted that the interpretation of the band at  $10.4\text{ }\mu$ , as discussed in this article is different from that proposed by Glazebrook and Saville<sup>27</sup>, and Bateman, Glazebrook, Moore, and Saville<sup>28</sup>. These authors suggest that this band is due to substituted tetrahydrothiophenes which their studies with small molecules have indicated are formed during vulcanization. These tetrahydrothiophenes are reported to have bands near  $10.5$  to  $10.6\text{ }\mu$  and one of them also

is reported to have a band at  $10.44 \mu$ . Ebonite containing 32 per cent sulfur and squalene-polysulfide residue from distillation of the reaction product are also reported to have bands in this region in contrast to the results obtained under the conditions employed in the present work. It should be noted that the wavelength of the band observed at  $10.4 \mu$  in the present work is shifted to longer wavelengths with increased sulfur content and occurs at  $10.45 \mu$  with 25 per cent sulfur. This general trend is in agreement with the findings of Sheppard and Sutherland<sup>2</sup>. Furthermore, the spectrum of the squalene-sulfur reaction product in Figure 5 has a shoulder at  $10.5 \mu$ . It may be that the tetrahydrothiophenes produce the bands at the longer wavelengths and that the band at the shorter wavelengths near  $10.4 \mu$  is actually due to a shifted double bond. Perhaps the tetrahydrothiophenes form at a late stage of the reaction or under conditions of higher concentration of sulfur. In this connection Craig<sup>38</sup> has shown that tetrahydrothiophene itself does not react with maleic anhydride when the two are heated at  $125^\circ \text{C}$  for 90 min. Thus, the changes observed on reacting the squalene-sulfur reaction product with maleic anhydride, including removal of the band at  $6.25 \mu$  and a possible decrease in the intensity of the band at  $10.4 \mu$ , were probably not due to reaction with tetrahydrothiophenes. In the absence of some other interpretation, it is assumed that these changes are due to reaction with a conjugated hydrocarbon system.

#### SUMMARY

A knowledge of the structure of vulcanized rubber is essential to the interpretation of vulcanization and oxidation studies and the physical properties of the material.

In the present work an infrared study has been made of structures resulting from a number of different methods of vulcanization. Sulfur vulcanizates show the presence of a shifted double bond, originally observed by Sheppard and Sutherland. The presence of conjugated double bonds is also indicated. Accelerators such as tetramethylthiuram disulfide and zinc dibutyl dithiocarbamate increase the rate of the double-bond shift and reduce the amount of conjugated double bonds. Neither the double-bond shift nor conjugation is observed as a result of vulcanization with tetramethylthiuram disulfide alone, hydrogen sulfide and sulfur dioxide (Peachey process), a peroxide, or gamma rays. These result in a possible decrease in carbonyl structures, and in the case of the last three, possible increased absorption due to OH and ionized carboxyl groups.

Apparently, the double-bond shift and conjugation are primarily phenomena related to the use of elemental sulfur. The other vulcanization systems studied evidently involve different mechanisms. An implication of the present work is that there may be a relationship between the reported ease of oxidation of sulfur vulcanizates, accelerated vulcanizates, and sulfurless vulcanizates (tetramethylthiuram disulfide alone), which decreases in the order named, and the probable amount of conjugation in the compound, which decreases in the same order.

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# RADIATION CROSSLINKING OF RUBBER—EFFECT OF ADDITIVES \*

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Rubber is one of the linear polymers which may be crosslinked by high energy radiation. In this paper the effect of a range of additives on the crosslinking of rubber by pile and gamma radiation is reported. Many were found to retard crosslinking and this is of interest mechanistically and as an example of protection against high energy radiation.

A major problem in radiation chemistry is the relative importance of ions, excited molecules, and free radicals. An ionic mechanism has been suggested for the crosslinking of polyethylene<sup>1</sup> and both excitation transfer<sup>2</sup> and free radical<sup>3</sup> hypotheses of protection have been suggested in the radiolysis of polymethyl methacrylate. The adequacy of a free radical mechanism may be assessed by comparison of protective power and radical acceptance and in this work most of the additives were chosen because of their known, or reasonably inferred, reactivity towards free radicals and, in particular, of polyisoprenyl radicals<sup>4</sup>.

## EXPERIMENTAL MATERIALS AND METHODS

**Materials.**—Pale crepe was lightly masticated in air, then acetone extracted for 24 hours in nitrogen and dried *in vacuo* immediately before use. Rubber A (2.2% extract, 0.6% O, 0.3% N) had a limiting viscosity of 500 g<sup>-1</sup> ml in benzene. Rubber B (1.5% extract, 0.4% O, 0.2% N) was highly branched with a limiting viscosity number of 386 g<sup>-1</sup> ml in benzene and an osmotic molecular weight<sup>5</sup> ca. 10<sup>6</sup>. A butadiene-styrene copolymer (Polysar S-65) was used without purification. Additives were of analytical or ordinary laboratory reagent grade and were not further purified. 1,1-Diphenyl 2-picrylhydrazyl was kindly supplied by Dr. W. F. Watson (BRPRA)<sup>6</sup>.

**Preparation of mixtures.**—Four methods of mixing were used. (i) *Mastication.* Reproducible breakdown of the rubber was achieved as ascertained by the behavior of the masticated rubber in compression (Williams Plasticity: BS.903). The same criterion of breakdown is of doubtful validity in the presence of additive and it was preferred simply to subject the mixture to a standard mechanical treatment. The weighed additive was quantitatively incorporated during mastication in air on the twin roll mill. The temperature, as measured by an injection pyrometer, never rose above 30° C. Sheets were prepared by pressing the warmed mixtures between glazed cloth. (ii) *Diffusion.* Using a method due to Cunneen<sup>7</sup>, samples from sheets prepared as in (i) were swollen with a small amount of a benzene-acetone solution of the additive. After allowing 14 days, in nitrogen, for the additive to diffuse into the rubber, the samples were kept in a stream of nitrogen until free of solvent. (iii) *Casting from solution.* Sheets were cast in nitrogen from benzene solutions

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of rubber and additive. (iv) *Freeze drying.* Benzene solutions of rubber and additive were "freeze dried" immediately before use.

*Irradiation of samples.*—Samples were either wrapped in aluminum foil and packed in cans in nitrogen or degassed and sealed in glass tubes at  $<10^{-4}$  mm Hg. Radiation from the Harwell Pile (BEPO) comprises slow and fast neutrons and gamma rays; unit radiation was monitored by reference to an integral slow neutron flux of  $10^{17}$  slow neutrons/cm<sup>2</sup>.<sup>8</sup> The temperature during irradiation was about 70° C and 1 unit was administered in about 16 hours. Usually samples in different cans given the same nominal dose gave closely similar equilibrium swelling values but occasionally significant differences were observed. Therefore, comparisons were made among samples from a single can. When samples were separated only by aluminum foil there was some inter-contamination, but this did not obscure the relative effects of additives. Induced radioactivity in glass tubes used in occasional experiments caused delays in testing.

Co-60 sources of The Technological Irradiation Group (Harwell) provided almost monochromatic gamma radiation (1.25 Mev) at a nominal field intensity of 7000 rep/min with an ambient temperature of 25° C.

*Chain molecular weights.*—Irradiated samples were acetone extracted in nitrogen, and acetone then removed at ca.  $10^{-2}$  mm Hg. Equilibrium swellings of samples immersed in benzene for 48 hours at an ambient temperature of 25° C were determined either by the method of weighing or by measurement of dimensional increase. Chain molecular weights ( $M_c$  values) were calculated for convenience from the simpler of the Flory-Huggins equations<sup>9</sup>.

$$-In(1-V_r) = V_r - \mu V_r^2 = \rho V_0 M_c^{-1} V_r^{1/2}$$

or, for  $M_c$  values  $> 10^4$ , from the approximation

$$V_0 \rho V_r^{3/2} = M_c (0.5 - \mu)$$

In these equations  $V_r$  is the volume fraction of rubber in the swollen material,  $V_0$  the molar volume of the swelling liquid,  $\mu$  an interaction constant characteristic of the rubber and swelling liquid, and  $\rho$  the density of the rubber. A mean value was taken for  $\rho$  of 0.92 and  $\mu$  as .395<sup>10</sup> (more reliable  $\mu$  values have been established recently, in particular for the swelling of rubber in *n*-decane)<sup>11</sup>.

*Stress-strain curves.*—Incomplete dumbbells (BS.903: type C) were loaded at the rate of 100 g/min and the extensions measured.

*Fraction of crosslinks stopped.*—Protective power was expressed as  $F$ , the fraction of crosslinks stopped by the additive, calculated from

$$F = \left[ \left[ \frac{M_0}{(M_c)_1} - 1 \right] - \left[ \frac{M_0}{(M_c)_2} - 1 \right] \right] \left[ \frac{M_0}{(M_c)_1} - 1 \right]^{-1} \approx 1 - \frac{(M_c)_1}{(M_c)_2}$$

where  $M_0$  is the number average molecular weight of the rubber prior to cross-linking and  $(M_c)_1$  and  $(M_c)_2$  are the chain molecular weights of rubber and rubber with additive, respectively, when irradiated together. The approximation  $F$ , which is used with the present data, is justifiable when  $M_0 \gg (M_c)_1$ .

## EXPERIMENTAL RESULTS

Table I shows the effect of more than thirty fairly representative additives in stopping the pile crosslinking of rubber A. The concentration was equiva-

TABLE I  
F VALUES FOR PILE RADIATION

Additive	$M_e \times 10^{-4}$	F
2,4-Dinitrophenol <sup>1</sup>	15.37	.66
<i>o</i> -Phenylenediamine <sup>4</sup>	12.93	.63
Hydrazobenzene <sup>1</sup>	13.29	.61
Benzothiazolyl disulfide <sup>3</sup>	13.76	.60
1,2-Naphthoquinone <sup>1</sup>	12.72	.59
<i>o</i> -Nitrophenol <sup>1</sup>	11.47	.55
<i>m</i> -Dinitrobenzene <sup>5</sup>	11.47	.54
Benzoquinone <sup>1</sup>	10.37	.50
Benzoquinone <sup>4</sup>	9.19	.43
Catechol <sup>2</sup>	10.63	.49
Azobenzene <sup>1</sup>	10.09	.49
<i>N</i> -Phenyl-2-naphthylamine <sup>1</sup>	9.83	.47
$\beta$ -Naphthol <sup>1</sup>	9.83	.47
<i>m</i> -Nitrophenol <sup>1</sup>	8.74	.41
Diphenylamine <sup>2</sup>	8.74	.38
2,4-Dinitro aniline <sup>1</sup>	8.10	.36
<i>p</i> -Nitrophenol <sup>1</sup>	7.78	.33
<i>m</i> -Phenylenediamine <sup>4</sup>	6.63	.27
Unextracted rubber <sup>1</sup>	7.10	.27
Naphthalene <sup>1</sup>	5.88	.18
Naphthalene <sup>3</sup>	6.81	.20
Benzophenone <sup>4</sup>	5.88	.18
Benzophenone <sup>4</sup>	5.95	.22
Diphenyl <sup>4</sup>	5.99	.19
Benzoin acid <sup>3</sup>	6.12	.12
Pentaerithritol <sup>1</sup>	5.59	.07
Phenol <sup>2</sup>	5.76	.07
Phenol <sup>4</sup>	5.17	.06
Phenol <sup>5</sup>	5.26	0
Dodecyl alcohol <sup>1</sup>	5.39	.04
Anisole <sup>3</sup>	5.54	.03
Stearic acid <sup>1</sup>	5.13	0
Urea <sup>1</sup>	5.13	0
Phthalic anhydride <sup>3</sup>	5.31	-.03
Channel Black <sup>1*</sup>	5.17	-.05
<i>p</i> -Dichlorobenzene <sup>1</sup>	4.90	-.05
Furnace Black <sup>1*</sup>	4.90	-.11
<i>p</i> -Phenylenediamine <sup>4</sup>	4.90	-.10
<i>p</i> -Phenylenediamine <sup>4</sup>	4.58	-.12
Hexachlorobenzene <sup>3</sup>	4.65	-.12
Hexachlorobenzene <sup>3</sup>	3.62	-.15
Hexachloroethane <sup>3</sup>	4.37	-.13
Hexachloroethane <sup>3</sup>	4.57	-.15
Rubber <sup>1</sup>	5.17	
Rubber <sup>3</sup>	5.39	
Rubber <sup>3</sup>	5.45	
Rubber <sup>4</sup>	4.85	
Rubber <sup>4</sup>	5.26	

\* Rubber 100; black 2; by weight.

lent in moles to 2 per cent hydroquinone and the dose 0.16 unit. The F value was calculated by reference to the appropriate rubber  $M_e$  value which is indicated by the number in Table I. Incorporation of additive was by mastication using rubbers 1 to 4 and by diffusion with rubber 5. The trend of these results was confirmed by measurements of extension at constant stress but under conditions which did not justify a numerical check on the value of F. Further F values are given in Table II but in this case were obtained at a dose of 0.5 unit for rubber B sealed *in vacuo* (Method (iv)).

TABLE II  
*F* VALUES FOR PILE RADIATION

Additive	$M_e \times 10^{-4}$	<i>F</i>
1,1-Diphenyl-2-picrylhydrazyl	3.42	.66
Catechol	2.92	.48
Hydroquinone + air	2.49	.39
Hydroquinone	2.38	.36
1-Naphthoic acid	1.98	.23
Naphthalene	1.94	.22
Benzoic acid	1.90	.20
Resorcinol	1.80	.16
Air	1.76	.14
Dimethyl glyoxime	1.67	.09
No additive	1.52	

The effect of the concentration of some additives on equilibrium swelling was investigated. Incorporation of additive by mastication usually gave erratic results, those shown in Figure 1 being exceptions. The casting of sheets (Method (iii)) always gave consistent results some of which are shown in Figures 2 and 3. *F* values calculated for the maximum concentration, and sometimes for a second specified dose, are shown in parentheses.

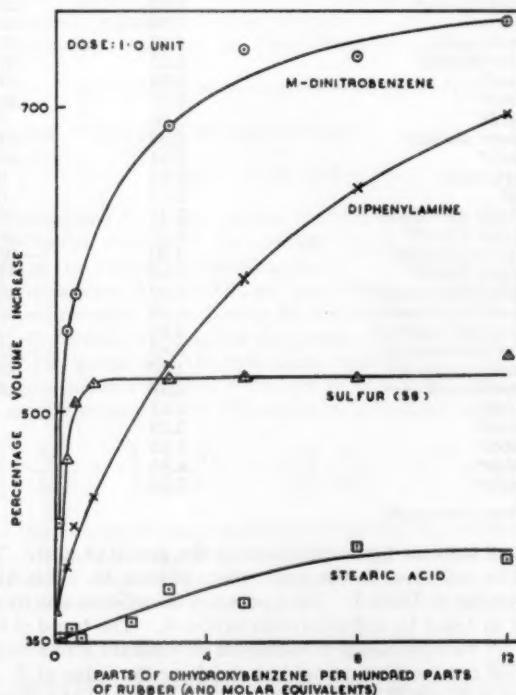


FIG. 1.—Concentration of additive and swelling.

Figure 4 shows the effect of a few chosen representative additives on the stress-strain properties of a butadiene-styrene copolymer. Equilibrium swelling values in benzene are shown in parentheses (% volume increase).

Table III gives swelling results obtained by  $\gamma$ -irradiation of rubber B *in vacuo* (Method (iv)).

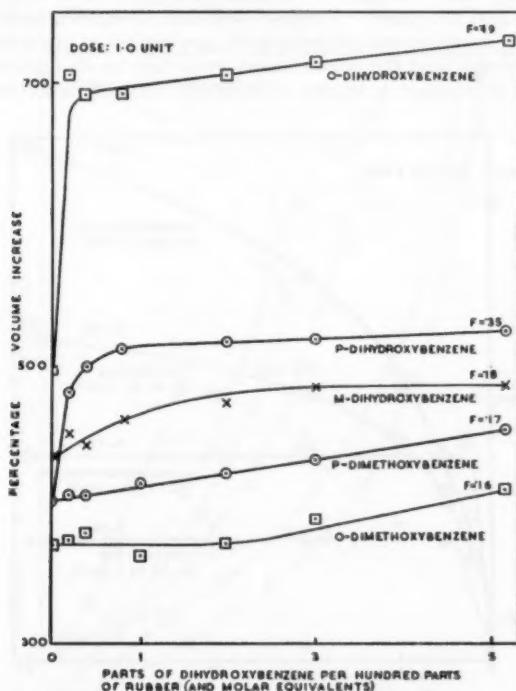


FIG. 2.—Concentration of additive and swelling.

## DISCUSSION

Charlesby<sup>12</sup> has reported that nearly all the gas evolved on exposing rubber to pile radiation is hydrogen. From the properties of the network formed he has also deduced that the ratio of main chain fractures to crosslinks is less than 0.1. In the presence of radical acceptor (methyl methacrylate and a polymerization inhibitor) the viscosity of rubber is not affected by gamma radiation in doses of up to at least  $10^6$  rep<sup>13</sup>. All these facts suggest that random main chain fracture is negligible in comparison with the breaking of carbon-hydrogen bonds. It will be shown later that a large proportion of the crosslinks, at least, are formed from free radicals. These facts are most simply related by supposing that effectively, the following reaction occurs  $RH \longrightarrow R\cdot + H\cdot$ , where RH represents rubber hydrocarbon. The polyisoprenyl radical ( $R\cdot$ ) has an obvious crosslinking potential and Bateman has discussed that of atomic hydrogen in

forming related radicals from rubber either by hydrogen abstraction or by addition to a double bond, in his work on photovulcanization<sup>14</sup>.

It is unlikely that any preferential fracture of bonds near the ends of a molecule, as has been found in the radiolysis of polymethylenes<sup>15</sup>, would be sufficiently important to significantly alter the  $F$  value with rubber.

*Protection by radical acceptors*<sup>4</sup>.—Considerable protection is conferred only by efficient radical acceptors. Further, inefficient acceptors, such as alcohols, certain phenols, aromatic and aliphatic acids, are inefficient protectors. Therefore, it is suggested that the predominant protective mode involves free radicals. Radical acceptance is known or inferred from the inhibition or retard-

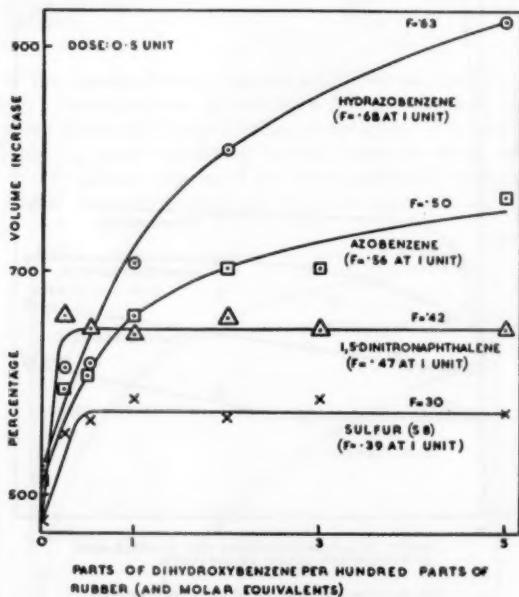


FIG. 3.—Concentration of additive and swelling.

ation of known radical reactions, e.g., quinones, disulfides, aromatic nitro compounds, and amines in polymerizations, and hydroquinones in oxidations. The acetone soluble fraction of rubber ( $F = .29$ : Table III) includes unknown radical acceptor<sup>16</sup>. The most relevant data on radical acceptance is that of Watson<sup>4</sup> on the efficiency of additives in consummating the shear induced scission of rubber molecules, which is a measure of their reactivity towards polyisoprenyl radicals of the type  $+CH_2-C(CH_3)=CH-CH_2$ . There is qualitative agreement with his results except that in his system the protective agents, sulfur and hydroquinone, were only very weak radical acceptors.  $F$  values for sulfur varied considerably with the reaction conditions but this is not surprising in view of its potentiality as a crosslinking agent. Protection by hydroquinone was considered in more detail, since it seems unlikely that it could be effective through competing with isoprene units for atomic hydrogen.

The data of Table II on rigorously outgassed rubber show that retardation by hydroquinone does not depend on its well-known reactivity towards peroxy radicals which might otherwise have been suspected of having a role in network formation. Instead, a more likely explanation of the difference is to be found in Table III which indicates that the effect of hydroquinone as a radical acceptor is swamped by the presence of the acetone soluble fraction, and hence under the conditions used in the work on shear-induced scission.

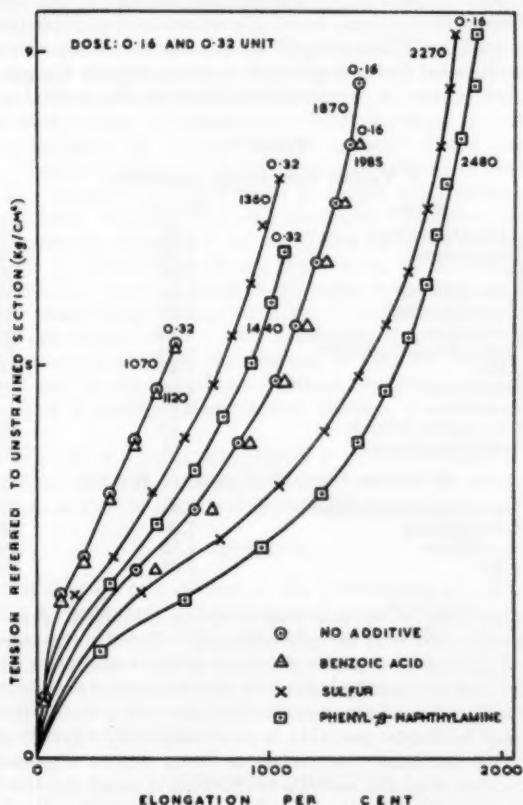


FIG. 4.—Additives in a butadiene-styrene copolymer.

The relatively small retarding effect of atmospheric oxygen ( $F = .14$ , Table II;  $F = .40$ , Table III) is probably controlled by the dose rate and its diffusion into the rubber<sup>17</sup>.

A convincing example of the ability of the free radical hypothesis to account for differences of structure on protective action is provided by the dihydroxybenzenes (Figure 2). The ortho and para are much more effective than the meta-isomer. A similar difference in reactivity has been reported by Bolland and ten Have<sup>18</sup> regarding the efficiency of these compounds as inhibitors of the

thermal oxidation of rubber hydrocarbon. It has been suggested that the ortho and para isomers are effective because of the readiness with which they form resonance stabilized semi-quinones. In extension of this supposition it would be expected that if the labile hydrogen atoms of the effective isomers are replaced by methyl groups, then reduced retardation of crosslinking would ensue. That this is so may be seen from the ortho- and para-dimethoxybenzene plots of Figure 2.

While the predominant importance of free radicals in the radiation crosslinking of rubber is likely, there is still the question of quantitative sufficiency. An argument used by Hinshelwood<sup>19</sup> to demonstrate a fractional nonradical reaction in the thermal decomposition of hydrocarbons in the gaseous phase is that the reaction cannot be completely inhibited by the radical acceptor nitric

TABLE III  
*F* VALUES FOR GAMMA RADIATION

Additive	$M_s \times 10^{-4}$	<i>F</i>
<i>m</i> -Dinitrobenzene	4.47	.75
Benzoquinone	1.79	.48
Air	1.84	.40
Hydroquinone	1.81	.39
Diphenylamine	1.63	.32
Anthracene	1.60	.31
Phenyl-2-naphthylamine	1.60	.31
Sulfur	1.24	.11
Benzoic acid	1.23	.10
No additive	1.10	—
<i>N</i> -Bromosuccinimide	.72	-.53
Hexachloroethane	.57	-.93

*F* VALUES USING UNEXTRACTED RUBBER

Phenyl-2-naphthylamine	2.00	.47
Hydroquinone	1.69	.35
No additive	1.55	.29
Sulfur	1.41	.22

oxide. The possibility of approaching complete inhibition of radiation crosslinking was investigated only for pile radiation. Even in the presence of large amounts of radical acceptor about one-third of the crosslinks are still formed. However, this is not necessarily indicative of a nonradical crosslinking reaction. Related observations have been made in the radiolysis of water where formation of hydrogen and hydrogen peroxide is not completely suppressed by radical acceptors<sup>20</sup>. This has been interpreted as being due to a general feature of radiation chemistry, that the radicals are formed in small clusters in which the radical density is too great for the acceptor to compete with radical combination during the early stages of diffusion. A further point mitigating against complete inhibition of network formation is that a radical acceptor does not necessarily destroy the crosslinking potential of the site with which it reacts. For example, benzoquinone probably gives RO——O, which might still form a crosslink by combination with *R*.

Insofar as network formation was not completely inhibited, the results do not exclude the possibility of some crosslinking by a nonradical mechanism, e.g., by ions. Neither can it be said that there is negligible protection by energy transfer. For example, it is not known whether *F* values of 0.2 and 0.3, re-

spectively, for naphthalene and anthracene are reasonable in terms of radical acceptance or whether their known roles as energy acceptors is of importance<sup>21</sup>. Furthermore, it may be calculated from Figure 3 that one molecule of 1,5-dinitronaphthalene stops more than half a crosslink. If it is accepted that, as in thermal crosslinking by peroxides<sup>22</sup>, crosslinks are formed by the dimerization of polyisoprenyl radicals then the simple radical mechanism of protection would be inadequate.

Notwithstanding possible qualifications of this kind it is clear that the free radical mechanism of protection can account for, at least, some two-thirds of the crosslinks formed in natural rubber by pile radiation. Preliminary experiments indicate also the importance of free radicals in a butadiene-styrene copolymer on gamma irradiation (Figure 4).

*Increased crosslinking.*—Davidson and Geib<sup>23</sup> increased the pile crosslinking of rubber by inclusion of boron, effective because of the nuclear reaction  $^{10}\text{B}(n, \alpha)^7\text{Li}$ . Burton<sup>24</sup> has concluded that an excited state of benzene- $d_6$  is able to sensitize the molecular elimination of hydrogen from cyclohexane when a mixture is irradiated with high velocity electrons. However, increased crosslinking as indicated by negative  $F$  values (Table I), is not necessarily attributable to any role of the additive during irradiation. For example it is known that certain aromatic diamines cause crosslinking in rubber<sup>25</sup>, and that network formation may ensue when various additives including halogen compounds and carbon blacks are sheared in<sup>4,26</sup>. Yet, confining attention to results obtained by mixing methods other than mastication, it may be concluded that hexachlorobenzene and hexachloroethane increase radiation crosslinking. Hexachloroethane had a similar effect in the absence of a neutron component (Table III).

The effectiveness of halogen compounds is understandable in view of their higher  $G$  (radical) values<sup>27,28</sup> than hydrocarbons and by analogy with their suggested role in activated photovulcanization<sup>29</sup>.

### SYNOPSIS

The effect of a range of additives on the crosslinking of rubber by pile radiation has been investigated. Retardation of crosslinking has been correlated with the reactivity of the additive towards free radicals. At least two-thirds of the crosslinks can be stopped by large amounts of radical acceptor. Preliminary results with a butadiene-styrene copolymer and with Co-60  $\gamma$ -radiation also indicate the importance of free radicals. Some halogenated compounds increased the degree of crosslinking.

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# CHANGES IN POLYSULFIDE CHAIN LENGTH IN SULFUR STRUCTURES OF VULCANIZATES BY LIGHT \*

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In previous work<sup>1</sup> we showed that sulfur vulcanizates of polybutadiene rubber (polysulfide<sup>2</sup> and thiuram<sup>3</sup> vulcanizates), which differ in their type of crosslinks, also differ in their stability to light. The best light stability is shown by a polysulfide vulcanize. The action of ultraviolet light in this case is accompanied by decomposition of sulfur bonds with the formation of a type of free sulfur which, in contrast to elemental sulfur, does not take part in photovulcanization processes, i.e., remains "inactive". Just what the nature of this inactive sulfur is, and the change in length of the polysulfide chains in the sulfur structures of the above-mentioned vulcanizates under the action of light, had not yet been established. Hence it was impossible to give a well-defined answer to the highly important question of why a polysulfide vulcanize has greater stability to light than a thiuram vulcanize. The present work is devoted to a study of this question.

Although the study of the types of sulfur bonds in vulcanizates is of considerable importance, no reliable methods for their determination are given in the literature. Ascertaining the nature of the bonds in a vulcanize by chemical methods involves great difficulties because of the impossibility of separating out the sulfur structures with different polysulfide chain lengths, as well as identical sulfur structures combined with the polymer in varying forms.

Thus, for instance, only the relative content of sulfur in the polysulfide form can be determined by the use of sodium sulfite<sup>4</sup> or methyl iodide<sup>5</sup>. It must be noted, however, that the results of an analysis by the use of  $\text{Na}_2\text{SO}_3$  are influenced in a complex way by the lengths of polysulfide chains and the nature of the radicals  $R_1$  and  $R_2$  in groupings of the type  $R_1-\text{S}_n-R_2$ . Since the nature of this influence is unknown, the results of such an analysis cannot be interpreted accurately, and this may sometimes lead to erroneous conclusions. Possibly this is the reason why the above method cannot successfully detect polysulfide structures in a thiuram vulcanizate<sup>6</sup>.

Similarly, the method of sulfur exchange reactions with the aid of radioactive sulfur<sup>7</sup>, and the thermochemical method<sup>8</sup> based on a study of stress relaxation in a vulcanizate at different temperatures, also do not permit a reliable determination of the lengths of polysulfide chains in the sulfur structures of the vulcanizates. Spectrophotometric methods have not been used specifically for the solution of the present problem. A previous study<sup>9</sup> is concerned with the infrared absorption spectrum of a natural rubber-sulfur vulcanizate. A weak band was detected at  $600 \text{ cm}^{-1}$ , which the authors attributed to the valency vibration of the C—S bond; no disulfide or polysulfide bonds were detected by

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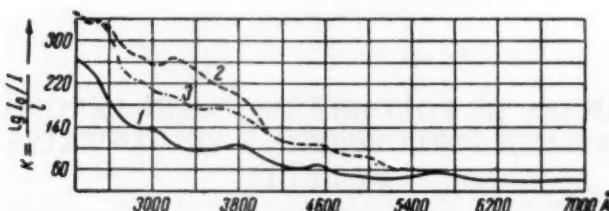


FIG. 1.—Absorption spectrum of a polysulfide vulcanizate in the ultraviolet and visible regions. 1—purified rubber; 2—extracted vulcanizate before irradiation; 3—extracted vulcanizate after 6 hours' irradiation. The abscissa represents the wavelength in Å, the ordinate light absorption.

them. Later<sup>10</sup> the infrared spectra of aliphatic sulfides and polysulfides were thoroughly studied. It was established that the valency vibrations of the C—S bond<sup>11</sup> (with a maximum at  $600\text{--}700\text{ cm}^{-1}$ ) and of the S—S bond<sup>12</sup> (with a maximum at  $430\text{--}490\text{ cm}^{-1}$ ) cause weak absorption bands in the infrared region.

Since, in addition to this, the concentration of sulfur bonds in soft vulcanizates is low and lies at the threshold of sensitivity of the infrared method, we cannot apply this method in our research. At the present time ultraviolet spectroscopy seems to offer greater sensitivity to differences between sulfur structures. It was shown in other work<sup>13</sup> that the maximum for *n*-cetyl sulfide is at 2250 Å, for *n*-cetyl disulfide at 2480–2520 Å, for *n*-cetyl trisulfide at 2500–2600 Å, for *n*-cetyl tetrasulfide at 2900–3000 Å; and for the hexasulfide, or for S<sub>8</sub> in alcohol or hexane, at 3200 Å and above. By comparing the data obtained in this work with other data<sup>14</sup>, one may conclude that the absorption bands of the different types of sulfur structures are very intense, are characteristic of a given type of structure and depend little on the nature of the remaining part of the molecule. As the polysulfide chain length increases, the absorption maximum shifts toward the region of the longer wavelengths of the spectrum.

In view of the above we considered the use of ultraviolet spectroscopy suitable for the study of changes in the lengths of polysulfide chains in the sulfur structures of polysulfide and thiuram vulcanizates under the action of ultraviolet light.

The experimentation was done with vulcanizates whose composition is given in the references<sup>2,3</sup>. These vulcanizates were tested in the form of films,  $10\mu$  thick, from which the free sulfur, the vulcanization accelerators and their decomposition products had previously been removed by extraction with a mixture of methanol and acetone for a period of 100 hours in an atmosphere of

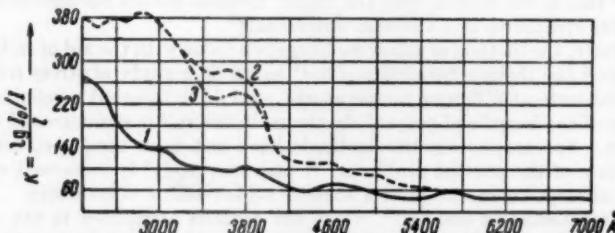


FIG. 2.—Absorption spectrum of a thiuram vulcanizate in the ultraviolet and visible regions. 1—purified rubber; 2—extracted vulcanizate before irradiation; 3—extracted vulcanizate after 6 hours' irradiation. The abscissa represents the wavelength in Å, the ordinate light absorption.

nitrogen. The vulcanized films were irradiated by filtered light from a mercury-quartz lamp, PRK-2, with wavelengths  $\lambda > 2900 \text{ \AA}$ , at a distance of 25 cm. The absorption spectra were read on a universal monochromator 3MP-2 in the region of 2200–7000  $\text{\AA}$ . A quartz prism was used in the monochromator system for ultraviolet light and a glass one for visible light.

The experimental method consisted of the following: spectra were obtained of films of polysulfide and thiuram vulcanizates (previously purified of their soluble ingredients by extraction), and then these films were irradiated for a period of 6 hours, extracted again after the irradiation for a period of 100 hours, and their spectra were read anew. In all cases the spectra were read on the same film in order to exclude any errors introduced by the experiment itself. The reproducibility between parallel experiments was satisfactory, the disagreement not exceeding 1%. In order to ascertain the polysulfide chain length in the free sulfur formed by the decomposition of the sulfur bonds of a polysulfide vulcanizate during irradiation, the spectrum of the free sulfur was examined in alcohol solution, and for comparison purposes the spectrum of elemental sulfur was also examined in alcohol solution. The results of this experiment are given in Figures 1–3.

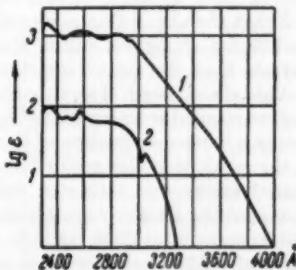


FIG. 3.—Ultraviolet absorption spectra of: 1—elemental sulfur ( $S_8$ ) in alcohol; 2—inactive sulfur (formed in the process of decomposition of the sulfur bonds in a polysulfide vulcanizate during irradiation) in alcohol. The abscissa represents the wavelength in  $\text{\AA}$ , the ordinate  $\log \epsilon$ .

As the data of Figure 1 show, an increase in absorption intensity in the range of 2200–5400  $\text{\AA}$  is observed in the spectrum of the polysulfide vulcanizate, Curve 2, as compared with that of pure rubber, Curve 1. This is explained by the presence of sulfur structures with varying polysulfide chain lengths in the polysulfide vulcanizate. The maximum observed in the region of 2300–2500  $\text{\AA}$ , Curve 2, is characteristic of monosulfides and disulfides. The maximum at 3250  $\text{\AA}$  is characteristic of hexasulfides. Absorption in the longer wavelength regions ( $> 3400 \text{ \AA}$ ) indicates that the vulcanizate has polysulfides of a higher order. The irradiation of a polysulfide vulcanizate is accompanied by a decrease in absorption intensity (Figure 1, Curve 3). This decrease is due to the decomposition of polysulfide bonds, and thus polysulfides of a higher order are less stable to light.

In Figure 2 the absorption maximum for a thiuram vulcanizate, in the region of 2500–2600  $\text{\AA}$ , Curve 2, corresponds to the presence of disulfides and trisulfides in the vulcanizate. The absorption maximum in the region of 2800–2900  $\text{\AA}$ , Curve 2, indicates the presence of tetrasulfides. The drop in absorption in the long wavelength region attests that the content of higher polysulfides is negligible. Irradiation of a thiuram vulcanizate is accompanied by the de-

composition of polysulfide bonds, mainly of hexasulfides and sulfides of a still higher order (in the region of 3200–4000 Å).

A comparison of Figures 1 and 2 shows that a thiuram vulcanizate gives a more intense absorption in the ultraviolet and visible regions than a polysulfide vulcanizate, although the thiuram vulcanizate contains only one-fourth as much combined sulfur as the polysulfide vulcanizate. This can apparently be explained by the difference in the distribution of the combined sulfur in the sulfur structures. It is known<sup>15</sup> that the intensity of the absorption band of the sulfur structures is different. The maxima here are: hexasulfide, 3200 Å ( $\log \epsilon = 4.0$ ); the trasulfide, 2900–3000 Å ( $\log \epsilon = 3.39$ ); trisulfide, 2500–2600 Å ( $\log \epsilon = 3.22$ ); disulfide, 2480–2520 Å ( $\log \epsilon = 2.63$ ); and sulfide, 2250 Å ( $\log \epsilon = 2.2$ ). The intense absorption band observed at 3250 Å in the polysulfide vulcanizate indicates its relatively high hexasulfide content, while the minimum in the region of 2900–3000 Å indicates that the amount of tetrasulfide is negligible. The drop in the wavelength regions of 2480, 2500 and 2600 Å indicates that the relative disulfide and trisulfide content is low. A different situation is noted in the thiuram vulcanizate, however; it apparently contains a large amount of monosulfides, disulfides, trisulfides and tetrasulfides, while the higher sulfides are apparently present only in small amounts in this vulcanizate.

It is seen from Figure 3 that the absorption region of inactive sulfur is in the range of 2200–3200 Å, while for elemental sulfur this region is much wider (2200–4000 Å). This attests that the sulfur structures which form inactive sulfur have a lower polysulfide chain length than those forming elemental sulfur. Since the vulcanizates that we studied were irradiated by ultraviolet light with a wavelength  $\lambda > 2900$  Å, only a limited activation of the inactive sulfur has taken place in this region, with the result that this sulfur failed to bring about photo-vulcanization; the elemental sulfur was activated sufficiently in this region, however, and hence it promoted the photovulcanization of the rubber.

An examination of the experimental data leads to the conclusion that the higher light stability of the polysulfide vulcanizate as compared to the thiuram one is explained by the differing ultraviolet light absorption of the respective sulfur structures in these vulcanizates.

#### ACKNOWLEDGMENT

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# THE MECHANISM OF VULCANIZATION IN THE PRESENCE OF 2-MERCAPTOBENZOTHIAZOLE \*

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The mechanism of the action of one of the most widely used vulcanization accelerators, 2-mercaptopbenzothiazole (MBT), has not been sufficiently investigated. It was demonstrated by Wistinghausen<sup>1</sup>, and also Dogadkin and Pevzner (1951) that MBT is consumed during vulcanization, but the quantitative relationships involved in this reaction could not be established due to the lack of a method for determining the disappearance of the MBT.

For the present study we made use of MBT labeled with the radioisotope S<sup>35</sup> in the thiazole ring.

The synthesis of MBT was carried out in the following manner. First, MBT labeled in both sulfur atoms, was prepared<sup>2</sup> from phenyl isothiocyanate and elementary S<sup>35</sup>. The MBT thus obtained was then heated in sealed ampules with excess ordinary sulfur at 140° for 6 hours. Under these conditions, the interchange reaction between the elementary sulfur and the sulfhydryl sulfur leads to an equilibrium<sup>3</sup>. There was a twofold drop in the activity of the synthesized MBT. That is the way in which the labeling of the benzothiazole radical alone was accomplished, so that the radioisotope S<sup>35</sup> introduced into the MBT molecule was not exchanged with elementary sulfur under the vulcanization conditions that obtained. This now made possible simultaneous measurements of the rate of sulfur addition and the rate with which the accelerator is added to the rubber.

Vulcanization was investigated in compounds of natural rubber (NK), extracted and precipitated from benzene solution, and of sodium-butadiene rubber (SKB). The composition of the compounds is given in Table I. Following extraction with acetone, the combined sulfur in the vulcanizates as well as the free sulfur + the sulfur in the unused accelerator in the extract was determined by oxidation<sup>4</sup> with HNO<sub>3</sub> and Br<sub>2</sub> in the presence of MgO. The MBT combining with the rubber was determined by the radiometric method<sup>5</sup>. From the maximum swelling of the vulcanizates in xylene, we calculated the number of crosslinks in conformance with the Flory-Rehner equation<sup>6</sup>.

Figure 1 presents data relative to the kinetics of the addition of sulfur and MBT, in the vulcanization of NK at 121°. The reactions of sulfur addition and accelerator addition to rubber run a parallel course. In the presence of ZnO, a more intensive accelerator addition was observed, while at the same time the rate of sulfur addition did not appear to be influenced by the activator.

A small quantity of MBT added chemically to the rubber during stock preparation on the mill. In order to investigate the mechanism of this reaction of MBT with rubber on the mill, purified NK (rubber purified through cold extraction with acetone in a purified nitrogen atmosphere for 20 hours) was

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processed on the rolls for 20 minutes in the usual manner—except that atmospheric oxygen was excluded—with one part by weight of pure MBT being added. Then the masticated rubber was separated into fractions, by lowering the temperature of the solution, in a binary solvent (benzene-methyl alcohol).

TABLE I

Composition of compound		Vulcani- zation temp., °C	Vulcani- zation time, min	Combined elementary sulfur, g atoms/ g · 10 <sup>4</sup>	Combined MBT, mole/ g · 10 <sup>4</sup>	No. of cross- links, mole/ g · 10 <sup>4</sup>	Number or re- acted molecules of MBT required for each double bond
Natural rubber	100	121	0	—	1.00	—	—
S	4		20	3.52	2.84	6.27	0.29
MBT	2		40	5.10	3.16	8.97	0.24
			60	5.65	3.72	10.80	0.25
PBNA	1		80	6.22	4.11	10.26	0.30
ZnO	5		100	7.16	4.12	10.88	0.28
Stearic acid	2		120	8.38	4.22	14.0	0.23
SKB	100	140	0	—	0.37	—	—
S	2		5	3.88	0.47	0.45	0.20
MBT	1		10	5.04	0.56	0.91	0.20
PBNA	1		20	5.97	0.92	1.20	0.45
			30	5.95	1.38	1.60	0.63
			40	5.95	1.36	1.66	0.59
			60	6.11	1.66	2.19	0.58

The viscosity of each fraction was determined in benzene and the proportion of added MBT was determined radiometrically. From the data presented in Table II it is evident that the amount of combined MBT is increased to a certain extent with increase in the serial number of the fraction, that is, with

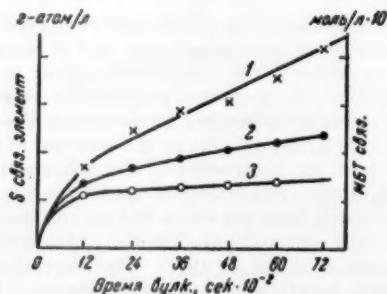


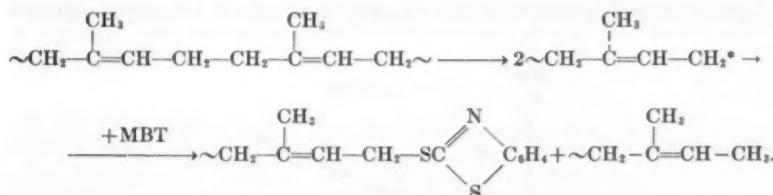
FIG. 1.—The kinetics of addition of sulfur and MBT during the vulcanization of natural rubber. Left hand ordinate is g atoms combined S per 1. Right hand ordinate is moles per 1 × 10<sup>4</sup> combined MBT. The abscissa is vulcanization time in seconds × 10<sup>3</sup>. Curve 3 is for sulfur addition, Curve 2 MBT addition in the presence of ZnO, and Curve 1 MBT addition in the absence of ZnO.

diminution in molecular weight. The phenomenon might also be explained by the fact that the addition of MBT to the polymer radical occurred through mechanical cleavage. Scission of the rubber chain in all probability takes place at the bond site connecting the allyl groups, inasmuch as this bond is

TABLE II

No. of fraction	$I/I_0$	Amount of combined MBT mole/l. $\times 10^4$	[%]
Unfractionated	—	—	—
1	0.053	3.21	12.0
2	0.091	5.45	27.0
3	0.110	6.22	24.5
4	0.071	4.28	9.2
5	0.090	5.39	8.0

weakened through the effect of the linking to about 45 kcal/mole. The original radicals react with the MBT molecule, apparently according to the scheme:



For this reason the MBT content in the low molecular weight fraction substantially exceeds that in the high molecular weight fraction. Should the locus of MBT reaction be the double bond, then a dependence of its disappearance on the plasticity of the rubber fraction probably would not be observed. In the scheme presented MBT reacts as a thiol; this thiol reaction leads, moreover, to the same result, regardless of the distribution in the fraction.

The addition of MBT to rubber during milling also has an accelerative effect on the vulcanization process, but to a substantially reduced degree.

Figure 2 shows the kinetics of the addition of sulfur and MBT during vulcanization of SKB. In this instance it was also observed that there was kinetic correspondence between the curves for the addition of sulfur and of MBT. At

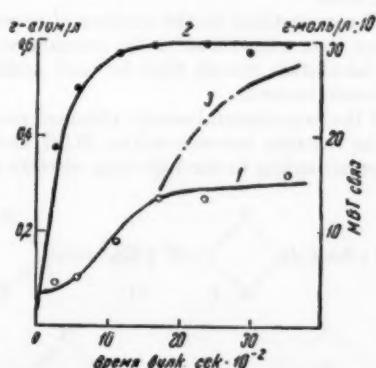


FIG. 2.—The kinetics of addition of MBT (Curve 1) and sulfur (Curve 2) during vulcanization and of sulfur (Curve 3) after the introduction by diffusion from solution of 2% sulfur. The left hand ordinate is g atoms per l and the right hand ordinate is g moles  $\times 10^4$  per l of combined MBT. The abscissa is vulcanization time in seconds  $\times 10^{-4}$ .

the moment the sulfur is completely combined (30 min) there is a sharp deceleration in the speed of addition of MBT, even though the concentration of the latter in the mixture is still sufficiently high. This fact indicates, then, that the reaction of MBT with rubber takes place at considerable speed only in the presence of sulfur, this being in agreement with the results we obtained<sup>7</sup> in regard to the catalytic action of sulfur when mercaptans add to olefins. In reality our experiments show that supplemental incorporation of sulfur into the vulcanized product as the latter is swelling (during the free sulfur-disappearance phase) leads to a new acceleration in the reaction taking place between MBT and rubber (Figures 2 and 3).

The kinetics of sulfur addition to rubber can be satisfactorily set forth by an equation for a first order reaction with respect to sulfur concentration. The kinetic constants derived from this equation demonstrate a linear dependency

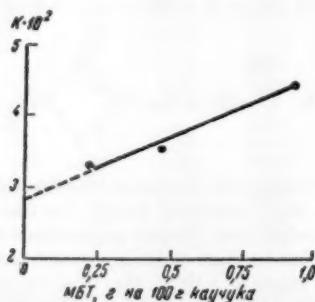
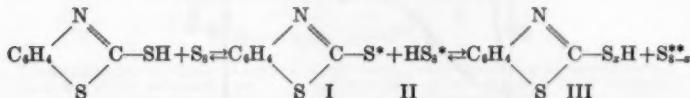


FIG. 3.—Dependence of the kinetic constant of sulfur addition on MBT concentration. The abscissa is g MBT per 100 g rubber.

on the MBT concentration (Figure 3). The activation energy of SKB vulcanization, using the conventional proportions of sulfur and accelerator, amounts to 20.6 kcal/mole.

The ratio of MBT consumption to the number of crosslinks (see Table I) is substantially smaller than unity, and, in the primary vulcanization period, remains constant. Calculation reveals that for each addition of accelerator, approximately two crosslinks occur.

A consideration of the experimental results obtained points to a uniformity in the character of the reaction between sulfur, MBT and rubber. This reaction apparently goes according to the following, already suggested<sup>8</sup>, scheme:



Under vulcanization conditions the radical  $\text{C}_6\text{H}_4-\begin{array}{c} \text{N} \\ \diagdown \\ \text{S} \\ \diagup \\ \text{C}-\text{S}^* \end{array}$  either abstracts



hydrogen from the alpha-methylene groups of the molecular chains of rubber to form MBT or is added to the double bonds. In either case, polymer radicals are formed that are capable of reacting with each other or with reactive groups of low molecular weight. The radical  $\text{HS}_n^*$  is added to the rubber molecule with resultant formation of polymeric mercaptans; the oxidation of the latter, or their reaction with the double bonds, leads to the formation of polysulfidic linkages among the rubber chains. The recombination of radicals I and II causes a dependence on the formation of 2-benzothiazolyl hydropolysulfide (III), resulting in a variable number of atoms of sulfur in the form of biradicals which immediately combine with the molecular chains of rubber at the double bonds.

In the complex series of vulcanization reactions cited the initial act seems to be the reaction of MBT with sulfur. For this reason the rate at which sulfur is combined with rubber, as already demonstrated, is a linear function of the MBT concentration.

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## THE EFFECT OF SWELLING ON THE STRENGTH OF VULCANIZATES \*

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Data on the influence of temperature, deformation conditions and swelling on the strength characteristics of high polymers are important in relation to the theory of the mechanism of the rupture of these materials. The relationship between the tensile strength of vulcanizates and the temperature and deformation rate<sup>1</sup> indicates the important role of intermolecular interaction in the mechanism of the rupture of high polymers with a spatial structure.

The observed relationships are difficult to explain if it is assumed that the resistance of a material to rupture is determined by principal chemical valency forces only. On the other hand, if the tensile strength of a vulcanizate is regarded as the sum of the principal valency forces  $P_z$  and intermolecular forces  $P_M$  all the known relationships between strength characteristics and the temperature and extension rate can be interpreted with a certain degree of approximation<sup>2</sup>. To determine the role of intermolecular forces in the mechanism of vulcanizate rupture it was of special interest to study the influence of swelling on tensile strength. This is a great practical as well as theoretical interest. The addition of substances of low molecular weight, known as softeners or plasticizers, to mixtures based on high polymers, is a widely used technological procedure. The substances used as plasticizers or softeners are generally well compatible with the polymers and can swell them.

Various chemical processes can take place between the plasticizers and the other ingredients in the production of a finished article from a raw mixture. In particular, softeners influence vulcanization and oxidation processes. Therefore in most cases a distinction must be made between chemical and physical interaction of plasticizers and the components of the mixture. The present paper deals mainly with the determination of the influence of physical interaction between the plasticizer and high polymer (swelling) on the tensile strength of vulcanizates.

One method whereby intermolecular interaction can be varied is swelling. This method is very convenient as by its means it is possible to vary intermolecular interaction without affecting interaction by the principal chemical valency forces. It is shown<sup>3</sup> that even in one and the same vulcanizate (and still more so in different vulcanizates) chemical and intermolecular bonds differing in nature and intensity are present. Consequently, different solvents should have different effects on the intermolecular interaction of a vulcanizate swollen in them. Therefore the materials chosen for the investigation were carbon-filled vulcanizates based on rubbers differing in chemical composition and structure, namely: natural (smoked sheet), butadiene-styrene (with 70:30 butadiene-styrene ratio), and butadiene-acrylonitrile (with 62:40 butadiene-acrylonitrile ratio); while the solvents used were dimethyl phthalate, dibutyl phthalate,

\* Reprinted from the *Colloid Journal* 19, 291-295 (1957); an English translation by Consultants Bureau, Inc. of *Kolloidnyi Zhurnal* 19, 287-292 (1957).

diethyl phthalate, dibutyl sebacate, diethyl sebacate, and vaseline oil. These substances differ both in molecular size and structure, and in polarity.

The swelling was effected by immersion of spade-shaped test specimens either directly in the solvent or in its alcoholic solution. To ensure uniform distribution of the solvent through the vulcanizate at different degrees of swelling, the specimens were kept between sheets of paper for 7-8 days after being extracted from the solvents and before the tensile tests. The degree of swelling was expressed in percentages on the weight of vulcanizate. The tensile and relative elongation tests were carried out according to State All-Union Standard 270-41. The number of parallel tests was not less than 25 in each case. The changes in the specimen dimensions caused by swelling were not taken into account in calculations of the cross section. The results for filled vulcanizates based on natural, styrene (SKS-30) and acrylonitrile (SKN-40) rubbers are

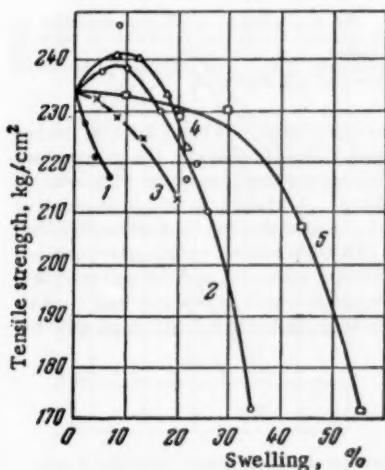


FIG. 1.—Variation of tensile strength of a filled natural rubber vulcanizate with the degree of swelling: 1) in dimethyl phthalate; 2) in dibutyl phthalate; 3) in diethyl phthalate; 4) in dibutyl sebacate; 5) in vaseline oil.

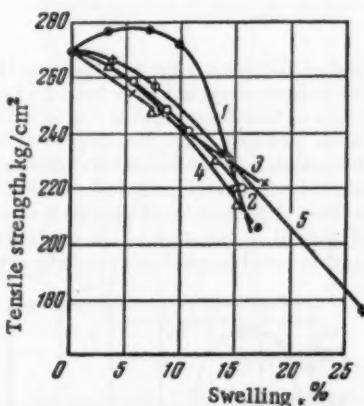


FIG. 2.—Variation of tensile strength of a filled SKS-30 vulcanizate with the degree of swelling: 1) in dimethyl phthalate; 2) in dibutyl phthalate; 3) in diethyl phthalate; 4) in dibutyl sebacate; 5) in vaseline oil.

given in Figures 1, 2, and 3, respectively. These figures show that the tensile strength varies in different ways for different combinations of vulcanizate and swelling agent. In some cases the often described steady decrease of tensile strength with increasing swelling is observed. This is found for a natural rubber vulcanizate swollen in dimethyl and diethyl phthalates, and for a SKS-30 vulcanizate swollen in dibutyl and diethyl phthalates and in dibutyl and diethyl sebacates (Figures 1, 2). In contrast to these typical cases, when filled vulcanizates of natural rubber are swollen in dibutyl phthalate and dibutyl sebacate, of styrene rubber in dimethyl phthalate, and of nitrile rubber in dimethyl, dibutyl, and diethyl phthalates and dibutyl sebacate, the tensile strength does not change steadily but passes through a maximum at a definite degree of swelling. When a natural rubber vulcanizate is swollen in dimethyl phthalate, the tensile strength falls sharply, while SKS-40 vulcanizates swollen in this solvent show an initial considerable increase of tensile strength. Di-

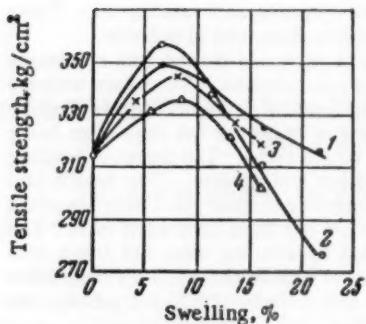


FIG. 3.—Variation of tensile strength of filled SKN-40 vulcanizate with the degree of swelling: 1) in dimethyl phthalate; 2) in dibutyl phthalate; 3) in dioctyl phthalate; 4) in dibutyl sebacate.

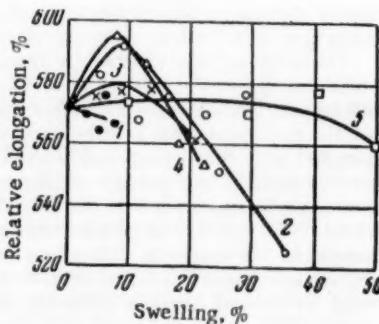


FIG. 4.—Variation of relative elongation of filled natural rubber vulcanizate with the degree of swelling: 1) in dimethyl phthalate; 2) in dibutyl phthalate; 3) in dioctyl phthalate; 4) in dibutyl sebacate; 5) in vaseline oil.

methyl phthalate is the most polar of the solvents used. When a natural rubber vulcanize is swollen in a less polar solvent, dibutyl sebacate, the greatest increase of tensile strength is found. The relative elongation of the vulcanizates varies similarly with the degree of swelling. A steady decrease of relative elongation is found for natural rubber vulcanizates swollen in dimethyl phthalate (Figure 4) and for butadiene-styrene (SKS-30) rubber vulcanizates swollen in dibutyl phthalate, dioctyl phthalate, dibutyl sebacate, and dioctyl sebacate (Figure 5). Variation of the relative elongation which passes through a maximum is found for swollen butadiene-acrylonitrile rubber (SKN-40) in all solvents

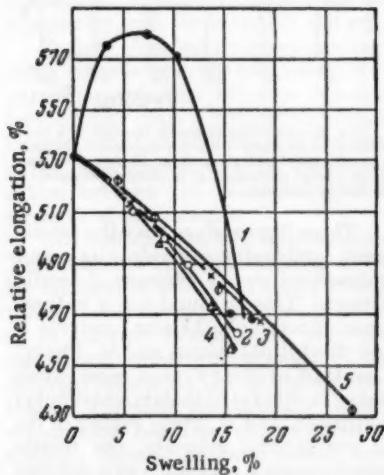


FIG. 5.—Variation of relative elongation of filled SKS-30 vulcanizate with degree of swelling: 1) in dimethyl phthalate; 2) in dibutyl phthalate; 3) in dioctyl phthalate; 4) in dibutyl sebacate; 5) in dioctyl sebacate.

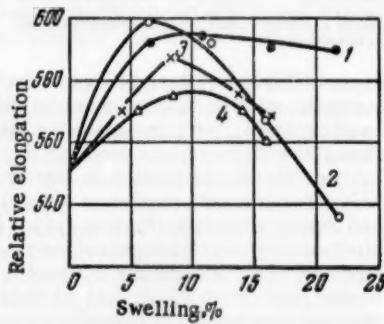


FIG. 6.—Variation of relative elongation of filled SKN-40 vulcanizate with degree of swelling: 1) in dimethyl phthalate; 2) in dibutyl phthalate; 3) in dioctyl phthalate; 4) in dibutyl sebacate.

(Figure 6). The curves in Figure 7 show that the variations of tensile strength and elongation at break for swollen vulcanizates follow a similar course.

Thus, the steady variation of static strength and relative elongation of swollen vulcanizates, described in the literature, is only a particular case of the influence of solvents on the mechanical properties of vulcanizates. Cases of unsteady variation, with increasing strength at low degrees of swelling, such as described here, are met quite often.

This course of strength and relative elongation variations during swelling of vulcanizates can be explained as follows. Swelling, on the one hand, increases the flexibility of the chain molecules, which facilitates their orientation during extension and therefore increases the tensile strength of the specimen.

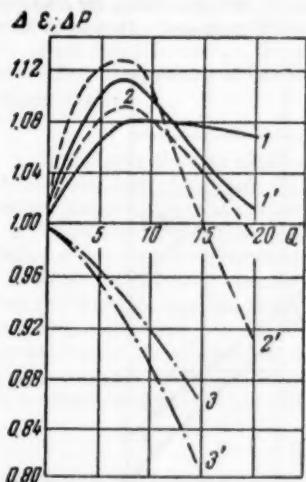


FIG. 7.—Relative changes of tensile strength and elongation at break for different degrees of swelling: 1) SKN-40 in dimethyl phthalate; 2) SKN-40 in dibutyl phthalate; 3) SKS-30 in dibutyl sebacate (the symbols 1, 2, 3, and 1', 2', 3' refer to the tensile strength and relative elongation, respectively).

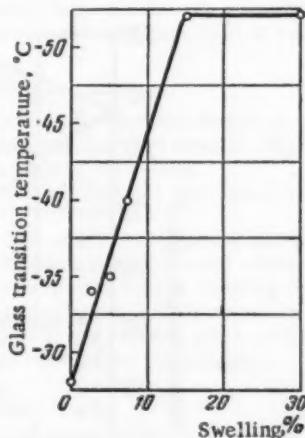


FIG. 8.—Variation of the glass transition temperature of SKN-26 vulcanize with degree of swelling in dibutyl phthalate.

A direct relationship between the degree of orientation (in the limit, the degree of crystallization) and strength of vulcanizates has been demonstrated in a series of papers<sup>4</sup>. On the other hand, penetration of the solvent molecules during swelling weakens the forces between the molecular polymer chains, leading to a decrease of the vulcanizate strength. The consequence of the superposition of these opposing influences is that, in the general case, the relationship between strength and degree of swelling will show extreme values. If the positive influence of the chain flexibility increase prevails, an increase of strength and elongation at break will be found at low degrees of swelling.

In the experiments described this was the case for butadiene-acrylonitrile rubber, the molecular chains of which are less flexible than those of natural rubber, swollen in all the solvents used. In the case of natural rubber the increase in chain flexibility as the result of swelling is slight, and for most solvents the more pronounced effect is decrease of strength owing to decreased energy of

intermolecular interaction. Natural rubber vulcanizates show decreases of strength and relative elongation even at low degrees of swelling. Natural rubber has high chain flexibility and the action of solvents on it largely consists of changes in the energy of interaction between the molecular chains.

The effect of changes of molecular chain flexibility on the strength of swollen vulcanizates becomes evident when Figures 3 and 8 are compared. It is seen that the glass transition temperature, which characterizes molecular chain flexibility, falls up to 12% swelling; further addition of solvent does not lower the glass transition temperature. The strength maximum corresponds to the degree of swelling which gives the lowest glass transition temperature.

It must be pointed out that, as has already been reported by us<sup>5</sup>, maximum values of tensile strength and relative elongation during swelling are also found in the case of fatigue (dynamic) strength of vulcanizates. It was to be ex-

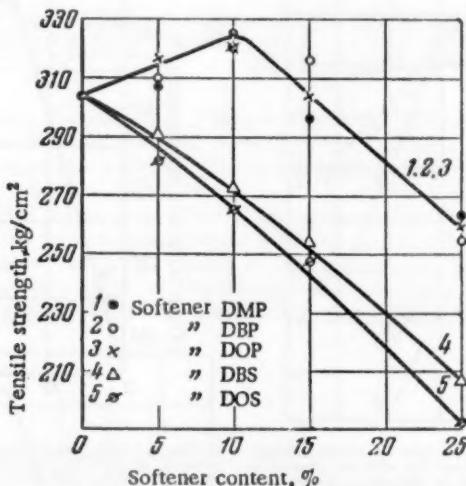


FIG. 9.—Variation of tensile strength of butadiene-acrylonitrile rubber vulcanizates with amounts of softener added during milling: 1, 2, 3) dimethyl, dibutyl, and dioctyl phthalates; 4) dibutyl sebacate; 5) dioctyl sebacate.

pected that similar maxima in the influence of the solvent on strength and relative elongation would be found when the solvent (softener) is introduced into the composition during milling before vulcanization. In fact, as Figure 9 shows, when such softeners as dimethyl, dibutyl, and dioctyl phthalate are added to a butadiene-acrylonitrile SKN-40 rubber composition, the strength-softener content curve shows a maximum. The strength maximum lies in the region of softener concentration ( $\sim 10\%$ ) corresponding to the strength maximum for the swollen vulcanizate. Additions of dibutyl and dioctyl sebacate result in steady decrease of strength with increasing softener concentration. Thus, the low molecular compounds act similarly as softeners (plasticizers) and as swelling agents. However, since softeners introduced into the composition may interact chemically with its ingredients during vulcanization, the results of their action on the mechanical properties of the vulcanizate evidently will not coincide completely.

The effect of swelling of vulcanizates on their strength characteristics, caused by the influence of swelling on the molecular chain flexibility, degree of orientation, packing density, energy of intermolecular interaction, and other parameters, is primarily determined by the molecular characteristics of the rubber-solvent (softener) pair. Unfortunately, the attempts to correlate the swelling effect with various molecular characteristics of the components of the system, which have been reported in the literature, have not yielded sufficiently definite results. We found the following values for the dielectric constants of the solvents (swelling agents) studied: dimethyl phthalate 6.56; dibutyl phthalate 5.03; dioctyl phthalate 4.17; dibutyl sebacate 3.71; dioctyl sebacate 3.37.

It is not possible to correlate the dielectric constant of a solvent with the effects of its action on the strength characteristics of swollen vulcanizates<sup>6</sup>. There is no doubt that, in addition to the polarity of the solvent and the magnitude of the cohesive energy, the size and configuration of the solvent molecules which affect the packing of the rubber molecules are also important in relation to these effects.

#### SUMMARY

1. It is shown that, in addition to the previously described steady decrease of tensile strength of vulcanizates during swelling, there are cases in which the strength passes through a maximum at low degrees of swelling.

2. Variations of a similar character during swelling are also found for the relative elongation of vulcanizates.

3. Such variations of tensile strength and relative elongation are found when the increase of chain flexibility and the associated increased orientation effect is greater than the effect of weakened intermolecular bonding in the polymer caused by penetration of the solvent molecules into the polymer.

4. A strength maximum may also be found if the swelling agent (softener) is introduced into the rubber composition on rolls before vulcanization.

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- <sup>3</sup> Dogadkin, B., *Trans. III All-Union Conf. Colloid Chem.*, Acad. Sci. USSR Press, 1953, p. 136.
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# THE CHEMISTRY OF VULCANIZATION. I. DIPHENYL-METHANE AS A MODEL OF RUBBER HYDROCARBON FOR ITS REACTION WITH SULFUR \*

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## INTRODUCTION

Following the discovery of vulcanization of rubber by Goodyear, a vast number of experiments and speculations have been carried out, but the final clarification of the mechanism of vulcanization and acceleration has remained unsettled. Overemphasis of physical and technological criteria in the investigation of vulcanization may have contributed to the failure to attach importance to the purely chemical investigation. In fact rubber vulcanizates defy chemical investigation because they are insoluble and infusible.

However, in 1947 Farmer and collaborators<sup>1</sup>, using olefinic substances such as cyclohexene, dihydromyrcene and squalene as model compounds, proposed a new theory on the vulcanization of rubber by sulfur. According to them  $\alpha$ -methylenic hydrogen adjacent to olefinic double bonds is attacked by sulfur, and a hydrocarbon radical is formed. Then this radical couples with the diradical  $\cdot S_2 \cdot$  and this leads to polysulfides as primary reaction products. Farmer's theory laid the ground work for the chemical investigation of vulcanization but the reaction of olefins with sulfur is too complex to indicate the reaction mechanism.

Diphenylmethane (DPM) contains  $\alpha$ -methylenic hydrogen (to a benzene ring) and may be expected to react with relative readiness. Moreover the reaction of DPM with molecular oxygen is already reported<sup>2</sup> to produce water, diphenylmethyl hydroperoxide, tetraphenylethane and benzophenone. It is expected then that when DPM reacts with sulfur, it should give the thio analogs of these compounds. Since the reaction and reaction products of sulfur with DPM are considerably less complex than those with olefinic substances, the reaction mechanism should be elucidated by using the simpler hydrocarbon as a model compound. Comparative studies of the reaction with and without accelerator will present the key to the mechanism and theory of acceleration.

As fundamental studies of rubber vulcanization as well as acceleration the following are the two objects of this paper. The first is the reaction mechanism of DPM with sulfur at 180° C and the second is the pyrolysis of the primary product (dibenzhydryl polysulfide) to the secondary product (thiobenzophenone) at the same temperature.

Investigations on the reaction of DPM with sulfur in the presence of accelerators will be reported in other papers of this series.

## REACTION OF DIPHENYLMETHANE WITH SULFUR

*Experimental.*—Purified sulfur and diphenylmethane (DPM) (redistilled directly before use) were heated in a flask equipped with a condenser and an

\* Reprinted from the *Bulletin of the University of Osaka Prefecture*, Vol. 5, Series A, pages 161-167 (1957). Parts II-V follow in this issue.

TABLE I  
THE REACTION PRODUCTS OF DPM AND SULFUR AT 180° C

No.	DPM in mmoles; S in milligram atoms	Hour	Products in mmoles		
			H <sub>2</sub> S	PS	TBP
1		10	0.15	trace	0.05
2	200:400	20	0.60	0.1	0.44
3		30	1.14	0.21	0.87
4		50	1.55	0.48	1.05
5		10	0.66 (0.22)*	0.37	0.28
6	200:200	20	1.20 (0.14)	0.81	0.30
7		30	1.45 (0.008)	0.94	0.70
8		50	2.13	1.37	0.77

\* In parenthesis, H<sub>2</sub>S caught by lead acetate.

inert gas inlet tube. The latter two were ground jointed to the reaction flask. Throughout the reaction time the inert gas (carbon dioxide or nitrogen) was passed gently into the flask, and the hydrogen sulfide evolved was swept out through the condenser and absorbed in *N*/10-iodine solution. The iodine solution was titrated with thiosulfate after the reaction was completed. The reaction products other than H<sub>2</sub>S were distilled under diminished pressure (3 mm). Unreacted DPM distilled out at 95–105° C accompanied by thiobenzophenone (TBP) which had intense blue color. The TBP was converted to benzophenone by alcoholic potash, separated from DPM and identified as 2,4-dinitrophenylhydrazone. The distillation residues were sulfur and dibenzhydryl polysulfide (PS). PS, which was freed from sulfur as well as possible by acetone, was digested in acetone solution with saturated aqueous sodium sulfite solution for a long time, and then converted to dibenzhydryl disulfide. After the acetone was distilled out, white needles of disulfide separated; m.p. 152° C and mixed m.p. with an authentic sample 152° C. During the vacuum distillation of the reaction products of Experiments 5, 6 and 7 in Table I, the evolution of H<sub>2</sub>S was detected. An absorbing tower filled with solid lead acetate was inserted between the manometer and receiver of the distillation apparatus. Lead sulfide formed and was separated from unchanged acetate by hot water and weighed. H<sub>2</sub>S amounts caught by the lead acetate are tabulated in parenthesis in Table I, and the total H<sub>2</sub>S absorbed by iodine solution and caught by acetate are shown in Table I.

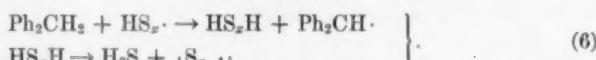
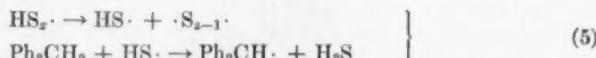
*Results and discussions.*—The reaction products and yields together with reaction conditions are summarized in Table I. The important relationship that the amount of H<sub>2</sub>S in mmoles is nearly equivalent to the amount of PS plus TBP is evident from Experiments 3–8. In Experiments 1 and 2 the amounts of products (PS and TBP) were too small to obtain a stoichiometric relation.

Experimental results thus lead to the mechanism indicated as follows. DPM is dehydrogenated by the sulfur diradical to produce diphenylmethyl radicals and HS<sub>2</sub><sup>·</sup>. This step is analogous to autoxidation and had been suggested already by Farmer<sup>1</sup>. Equations (2) and (3) or (4) indicate succeeding processes.



Thus, dibenzhydryl polysulfide (PS) is considered the primary reaction product. It was verified experimentally (see the next section) that PS forms TBP at 180° C.

Hydrogen sulfide must result from  $\text{HS}_x\cdot$ . The reason for this is as follows. Experiments showed that the reaction products at the higher sulfur dosage and at the shorter reaction time evolved considerable amounts of  $\text{H}_2\text{S}$  during vacuum distillation. This suggests that the hydrogen polysulfide ( $\text{H}_2\text{S}_x$ ) may be formed and remain in the reaction products. Bacon and Fanelli<sup>3</sup> confirmed that  $\text{H}_2\text{S}$  dissolved in molten sulfur and they found the solubility of  $\text{H}_2\text{S}$  to be higher, the higher the temperature of molten sulfur. This indicates that  $\text{H}_2\text{S}$  and sulfur form hydrogen polysulfide. In the present work, since  $\text{H}_2\text{S}$  was swept out by inert gas, the reversal of the case of Bacon and Fanelli occurs. Therefore, the mechanism of formation of  $\text{H}_2\text{S}$  is either Equation (5) or (6).



According to Equations (1), (2) and (3) or Equations (1), (2) and (4), two  $\text{HS}_x\cdot$  are required to produce one molecule of PS. On the other hand, according to Equation (5) or (6), two  $\text{HS}_x\cdot$  are equivalent to one  $\text{H}_2\text{S}$ . Therefore, PS in moles is equivalent to  $\text{H}_2\text{S}$  in moles.

According to Equations (18) and (19) or to Equation (20), which will be discussed in the next section, in order to produce one molecule of TBP from  $\text{Ph}_2\text{CHS}_x\cdot$ , one  $\text{HS}_x\cdot$  is required. Starting with DPM, two  $\text{HS}_x\cdot$  are required to produce one TBP. Thus, the yield of TBP in moles is also equivalent to that of  $\text{H}_2\text{S}$ . The important result is that the amount of  $\text{H}_2\text{S}$  evolved is nearly equal to that of (PS + TBP) and this can be interpreted by the mechanism indicated above.

#### PYROLYSIS OF BENZHYDRYL POLYSULFIDE

In the preceding section, the radical  $\text{Ph}_2\text{CHS}_x\cdot$  was assumed to form TBP. In order to verify this assumption, benzhydryl disulfide (DS) as well as the tetrasulfide (TS) was prepared and decomposed. In both cases the decomposition products were identified and estimated as far as possible.

*Preparation of benzhydryl sulfides.*—Thiobenzhydrol prepared from benzhydrol and thiourea hydrochloride, was extracted by benzene and oxidized to disulfide by iodine in alcohol. *Anal.*  $\text{C}_{26}\text{H}_{22}\text{S}_2$ : S% calcd. 16.09; found 15.82.

Thiobenzhydrol was distilled out at 98–99° C/0.03 mm Hg. A 10% solution of sulfur chloride in carbon tetrachloride was added dropwise to a 10% solution of thiobenzhydrol in carbon tetrachloride under nitrogen atmosphere. The mixture was cooled with ice and stirred for 4 hours. After the carbon tetrachloride was distilled out, ether was added to give after standing, a crop of crystals which was recrystallized from petroleum ether. *Anal.*  $\text{C}_{26}\text{H}_{22}\text{S}_4$ : C% calcd. 67.49, found 68.13; S% calcd. 27.72, found 27.16. Benzhydryl tetrasulfide thus prepared is considered to have a linear S—S structure<sup>4a</sup>, since sulfur chloride has a linear ClSSCl structure<sup>4b</sup>.

Benzhydryl monosulfide was prepared from thiobenzhydrol and diphenylbromomethane.

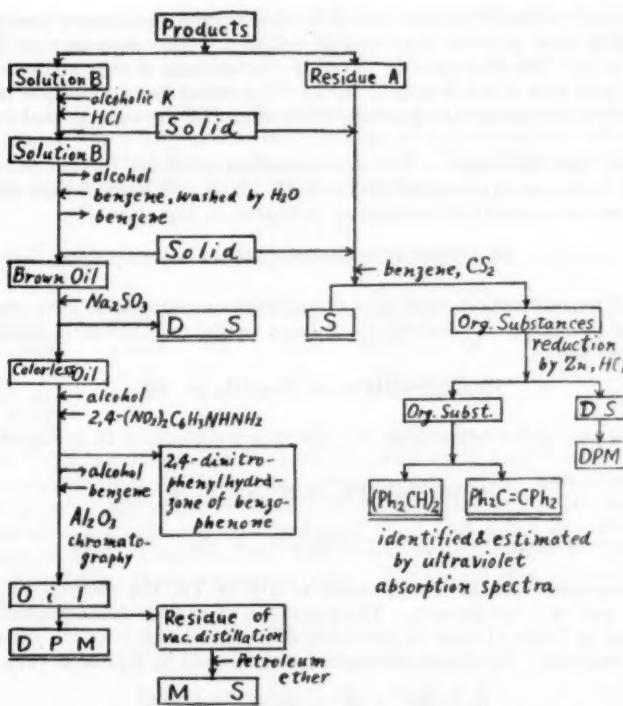


CHART 1.—Procedures to identify and estimate the reaction products.

*Method of pyrolysis and estimation of products.*—Methods of pyrolysis and determination of  $H_2S$  evolved were essentially the same as for the previous section. The decomposition products were dissolved in alcohol. Undissolved portion A and alcoholic solution B were separated. B was diluted to 100 cc, and in a 5 cc aliquot TBP was determined by Kitamura's method<sup>6</sup>. To another 10 cc aliquot  $N/20$ -iodine solution was added. Excess iodine was titrated with  $N/20$ -thiosulfate. This iodine consumption was attributable to  $H_2S$  which

TABLE II  
THE DECOMPOSITION PRODUCTS OF DS AND TS AT 180° C FOR 2 HOURS

Starting materials in mmoles	Products in mmoles								
	$H_2S$	TBP	Tetraphenyl-ethane	Tetra-phenyl-ethylene	MS*	DS	PS	DPM	S
DS (12.5)	0.53	3.63	3.02	trace	0.57	—	0.18	0.18	3.4
DS (12.5)	0.52	4.70	3.11	trace	0	—	1.20	—	1.25
DPM (25)									
DS (12.5)	0.54	9.49	0	0	0	—	1.38	0.53	—
S (50)									
TS (12.5)	0.90	12.72	0.07	trace	0	3.26	—	1.42	4.36

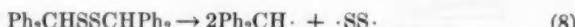
\* Benzydryl monosulfide.

remained in B, since B had no odor of thiobenzhydrol and since it precipitated lead sulfide with aqueous lead acetate solution. This showed that  $H_2S$  remained in B. The  $H_2S$  cited in Table II was the sum of that evolved during reaction and that which remained in B. The succeeding procedures required to identify and estimate the products other than  $H_2S$  are summarized in Chart 1.

*Results and discussion.*—The decomposition products formed at 180° C during 2 hours are summarized in Table II. It is well known<sup>6</sup> that disulfides decompose into mercaptyl radicals as indicated in Equation (7).



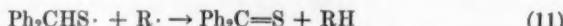
However, experiments showed that the disulfide or tetrasulfide gave some free sulfur on pyrolysis. Therefore, C—S bond fission must occur in addition to S—S bond fission.



In the case of the tetrasulfide, the first step is considered to be Equation (9) or (10).

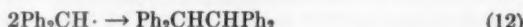


In the reaction mass in the pyrolysis of DS or TS, the radicals  $Ph_2CHS\cdot$ ,  $Ph_2CH\cdot$  and  $\cdot S_2\cdot$  are present. The formation of various decomposition products cited in Table II may be interpreted by consideration of the interaction of these radicals. Hydrogen abstraction is indicated in Equation (11).



In Equation (11),  $R\cdot$  represents  $Ph_2CH\cdot$  or  $\cdot S_2\cdot$ . Therefore, RH is  $Ph_2CH_2$  or  $HS_2\cdot$ . Radical  $HS_2\cdot$  acts as  $R\cdot$  again, and forms  $HS_2H$ . Hydrogen sulfide is formed from  $HS_2\cdot$  or  $HS_2H$ .

Recombination is indicated in the following equations.



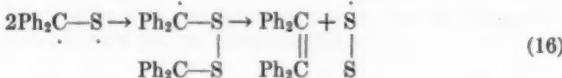
Polysulfide is formed by mutual recombination of  $Ph_2CHS_s\cdot$  or recombination of  $Ph_2CHS_s\cdot$  and  $Ph_2CH\cdot$  as indicated by Equations (3) or (4) cited previously. In the pyrolysis of TS considerable amount of DS was found as indicated in Table II. This DS results from recombination of radical  $Ph_2CHS\cdot$  produced in Reaction (9). The formation of tetraphenylethane is prevented in the presence of a sufficient amount of free sulfur as indicated by Equation (2). Benzhydrol monosulfide cannot be produced in the presence of a sufficient amount of free sulfur.

The mechanism of formation of a trace of tetraphenylethylene is illustrated by the following experiment. TBP, which was prepared by passing H<sub>2</sub>S and hydrogen chloride into an alcoholic solution of benzophenone under cooling and recrystallized from petroleum ether and dried in vacuum, was decomposed in the stream of nitrogen gas. The decomposition products are summarized in Table III. The purity of thiobenzophenone thus prepared was determined by Kitamura's<sup>5</sup> method and was found to be 81%. Considering the preparation method, the remainder might be benzophenone.

TABLE III  
THE DECOMPOSITION PRODUCTS OF TBP AT 180° C FOR 10 HOURS

Starting materials in mmole	Undecomposed TBP in mmole	H <sub>2</sub> S	Products in mmole				
			Tetraphenylethane	Tetraphenylethylene	DS	S	PS
TBP (10)	0.27	0	0	3.92	0	7.69	0
TBP (10)	3.63	0.10	trace	trace	0.40	0	0.12
DPM (191)							

From Table III, it is concluded that the pyrolysis of TBP forms 1 mole of tetraphenylethylene for each 2 gram atoms of sulfur. It has been already recognized by other investigators<sup>8</sup> that TBP exists in the excited triplet state. The facts that it can be readily autoxidized<sup>7,9</sup> and that it has an intense blue color support this. Therefore, the first step of decomposition of TBP is its excitation to triplet state (Equation (15)). The second step is indicated by Equation (16).



The results in Table III indicate that in the presence of excess DPM Reaction (16) is replaced by Reaction (17).

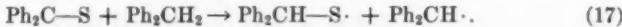


Table II also indicates that in the presence of DPM the amount of tetraphenylethylene approaches zero at 180° C. In the reaction mass of DPM and sulfur at 180° C, excess DPM and sulfur are always present. The formation of tetraphenylethane is suppressed by sulfur radicals by Reaction (2). Therefore, in the reaction product of DPM and sulfur at 180° C, neither tetraphenylethane nor tetraphenylethylene can be found. In the reaction of DPM and sulfur, the primary product is PS. Radical Ph<sub>2</sub>CHS<sub>x</sub>· decomposes to TBP as indicated in (11). Reaction (11) may be modified to (18) and (19).



If  $\cdot\text{S}_z\cdot$  does not take part in the decomposition of  $\text{Ph}_2\text{CHS}_z\cdot$  to TBP, the following reaction is obtained by adding Reactions (18) and (19).



#### SYNOPSIS

Diphenylmethane was used as a model of rubber hydrocarbon. Benzhydryl polysulfide, thiobenzophenone and hydrogen sulfide resulted from the reaction of it and sulfur at  $180^\circ\text{ C}$ . The amount of hydrogen sulfide was equivalent to that of polysulfide plus thiobenzophenone. Benzhydryl disulfide and tetrasulfide were synthesized and decomposed. From analogy to autoxidation and from experimental results, it was deduced that benzhydryl polysulfide is the primary product, and that thiobenzophenone is its decomposition product. The reaction mechanism is thoroughly discussed.

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## II. KINETICS OF HYDROGEN SULFIDE EVOLUTION DURING THE REACTION OF DIPHENYLMETHANE AND SULFUR \*

JITSUO TSURUGI

### INTRODUCTION

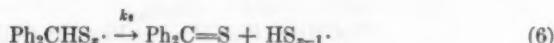
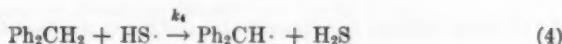
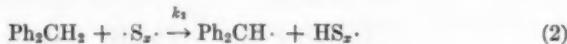
In Part I, the products and mechanism of reaction between diphenylmethane and sulfur were reported. The reaction products at 180° C were hydrogen sulfide, benzhydryl polysulfide (PS) and thiobenzophenone (TBP). On the basis of this mechanism the theoretical rate equation is now derived and compared with experimental results.

### CALCULATION OF THE RATE EQUATION FOR HYDROGEN SULFIDE FORMATION

Since the sulfur molecule has been shown to be an  $S_8$  puckered ring, the first step in the reaction process must be fission of the  $S_8$  ring.



Two or more reaction courses were considered in Part I for the evolution of  $H_2S$ . However, from the following course indicated by Reactions (1) to (7), the rate equation which coincides with experimental results can be obtained. Others and their consequent results will be mentioned later.



Applying the stationary state method, the following relations were obtained.

$$\begin{aligned} d[\cdot S_x \cdot] / dt &= k_1[S_8] - k_2[Ph_2CH_2][\cdot S_x \cdot] + k_3[HS_x \cdot] \\ &\quad - k_5[Ph_2CH \cdot][\cdot S_x \cdot] = 0 \quad (i) \end{aligned}$$

\* See preceding paper, this issue, for Part I. Part II is reprinted from the *Bulletin of the University of Osaka Prefecture*, Vol. 5, Series A, pages 169-172 (1957).

$$\frac{d[\text{Ph}_2\text{CH}\cdot]}{dt} = k_2[\text{Ph}_2\text{CH}_2][\cdot\text{S}_{z-1}] + k_4[\text{Ph}_2\text{CH}_2][\text{HS}\cdot] - k_5[\text{Ph}_2\text{CH}\cdot][\cdot\text{S}_z\cdot] = 0 \quad (\text{ii})$$

$$\frac{d[\text{Ph}_2\text{CHS}_z\cdot]}{dt} = k_5[\text{Ph}_2\text{CH}\cdot][\cdot\text{S}_z\cdot] - k_6[\text{Ph}_2\text{CHS}_{z-1}\cdot] - k_7[\text{Ph}_2\text{CHS}_z\cdot]^2 = 0 \quad (\text{iii})$$

$$\frac{d[\text{HS}_z\cdot]}{dt} = k_2[\text{Ph}_2\text{CH}_2][\cdot\text{S}_z\cdot] - k_3[\text{HS}_{z-1}\cdot] + k_6[\text{Ph}_2\text{CHS}_z\cdot] = 0 \quad (\text{iv})$$

$$\frac{d[\text{HS}\cdot]}{dt} = k_3[\text{HS}_z\cdot] - k_4[\text{Ph}_2\text{CH}_2][\text{HS}\cdot] = 0 \quad (\text{v})$$

In deriving the relations (i) to (v),  $\cdot\text{S}_z\cdot$  and  $\cdot\text{S}_{z-1}\cdot$  are assumed to be identical. The radicals  $\text{HS}_z\cdot$  and  $\text{HS}_{z-1}\cdot$  are also assumed to be equivalent. From (i), (ii) and (v),

$$[\cdot\text{S}_z\cdot] = k_1[\text{S}_8]/2k_2[\text{Ph}_2\text{CH}_2]$$

From (ii), (iii), (iv) and (v),

$$k_7[\text{Ph}_2\text{CHS}_z\cdot]^2 = 2k_2[\text{Ph}_2\text{CH}_2][\cdot\text{S}_z\cdot]$$

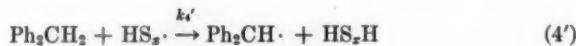
and then

$$[\text{Ph}_2\text{CHS}_z\cdot] = k_1^{\frac{1}{2}} \cdot k_7^{-\frac{1}{2}} [\text{S}_8]^{\frac{1}{2}}$$

The rate equation required can be derived as follows.

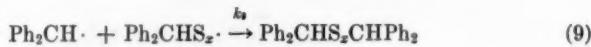
$$\begin{aligned} \frac{d[\text{H}_2\text{S}]}{dt} &= k_4[\text{Ph}_2\text{CH}_2][\text{HS}\cdot] \\ &= k_2[\text{Ph}_2\text{CH}_2][\cdot\text{S}_z\cdot] + k_6[\text{Ph}_2\text{CHS}_z\cdot] \\ &= k_1[\text{S}_8]/2 + k_6(k_1/k_7)^{\frac{1}{2}}[\text{S}_8]^{\frac{1}{2}} \end{aligned} \quad (\text{A})$$

As indicated in Part I, an alternative course for formation of  $\text{H}_2\text{S}$  is as follows.



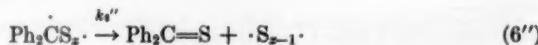
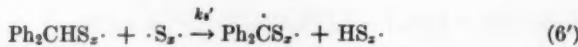
If (4') is substituted for (3) and (4), and if (8) is added to the other, the rate equation identical to (A) can be obtained by applying a like procedure.

An alternative step for formation of benzhydryl polysulfide was indicated in Part I.



If (9) is substituted in place of (7), the rate equation for  $\text{H}_2\text{S}$  formation cannot be derived.

Another course for formation of thiobenzophenone was indicated in Part I.



Replacing (6) by (6') and (6''), and assuming stationary states, the following rate equation can be derived.

$$d[\text{H}_2\text{S}]/dt = k_1[\text{S}_8]/2 + k_8'k_1k_2^{-1}k_7^{-1}[\text{S}_8]^{\frac{1}{2}}[\text{Ph}_2\text{CH}_2]^{-1/2} \quad (\text{C})$$

### EXPERIMENTAL RESULTS

A mixture of 50 mmoles of DPM and 6.25 mmoles of  $\text{S}_8$  (50 milligram atoms of sulfur) was heated in the stream of nitrogen gas. Hydrogen sulfide

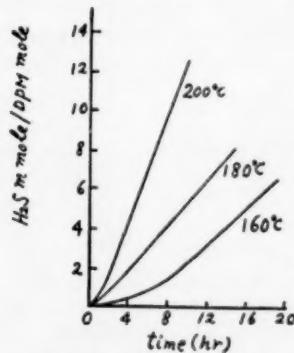


FIG. 1.— $\text{H}_2\text{S}$  evolved at various temperatures.

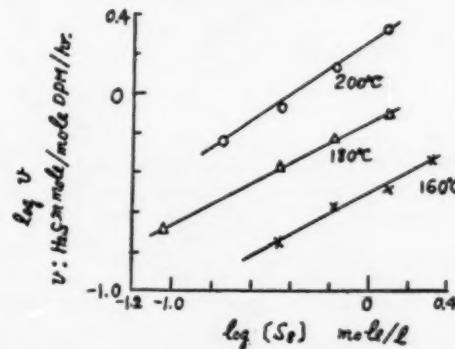


FIG. 2.— $\log v$  versus  $\log [\text{S}_8]$  at 160, 180 and 200° C.

evolved was absorbed in iodine solution and titrated by the same procedure as in Part I.  $\text{H}_2\text{S}$  yield versus reaction time is shown in Figure 1. Figure 1 shows that except for an induction period the rate of evolution of  $\text{H}_2\text{S}$  is constant. This result can be interpreted by considering that in reactions corresponding to (A) or (C) sulfur concentration is constant throughout the reaction time investigated. Table I in Part I and Figure 1 in this paper

TABLE I  
THE RATE OF HYDROGEN SULFIDE ( $v$ ) UNDER VARIOUS  
SULFUR CONCENTRATIONS

$\text{S}_8$ conc. in mmoles	0.914	0.1813	0.354	0.678	1.25	2.17
$v^*$ at 160° C			0.18	0.26	0.33	0.46
$v^*$ at 180° C	0.207		0.414	0.578	0.79	
$v^*$ at 200° C		0.572	0.85	1.378	2.21	

\* In mmoles/DPM, moles/hr.

show that sulfur consumption is small as compared with sulfur concentration used. Therefore the above assumption that sulfur concentration can be considered constant is justified. Directly from Figure 1 the rates of  $\text{H}_2\text{S}$  evolution are obtained. The rates ( $v$ ) thus obtained at 160, 180, and 200° C under various sulfur concentrations are tabulated in Table I.

In Figure 2,  $\log v$  is plotted versus  $\log [\text{S}_8]$ . Figure 2 indicates that the relation

$$v \propto [\text{S}_8]^n \quad (\text{D})$$

can hold at various temperatures and the values of  $n$  are 0.5, 0.53 and 0.7 at 160, 180 and 200° C, respectively. This result can be interpreted as follows. From the data of viscosity of molten sulfur<sup>2</sup>, it can be suggested that  $k_1$  has a very small value compared with  $k_6$  or  $k_7$  at 160° C or at lower temperatures. Then the relation  $k_1/2 \ll k_6(k_1/k_7)^{\frac{1}{2}}$  can hold and (A) reduces to the simpler (A').

$$v = k_6(k_1/k_7)^{\frac{1}{2}}[S_8]^{\frac{1}{2}} \quad (\text{A}')$$

Equation (A') coincides with experimental results at 160° C. Investigation of viscosity of sulfur also indicates that as the temperature rises, the fission of  $S_8$  ring becomes vigorous. Therefore, at higher temperatures,  $k_1$  has a greater value than  $k_6$  or  $k_7$ , and (A) reduces to another simpler equation:

$$v = k_1[S_8]/2. \quad (\text{A}'')$$

The experimental result that the value of  $n$  in (D) approaches unity as the temperature rises, can be interpreted by (A''). Thus, (A), (A') and (A'') interpret the experimental results satisfactorily, but (C) does not.

#### SYNOPSIS

Based on the reaction mechanism indicated in Part I, some rate equations of hydrogen sulfide evolved during the reaction of diphenylmethane and sulfur are derived. By comparing the theoretical equations with experimental results an equation which can interpret the results satisfactorily was selected and the most probable course of the reaction decided upon.

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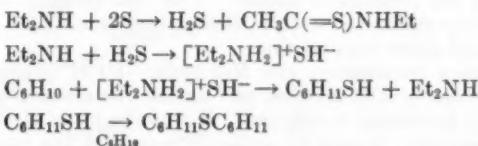
### III. THE ACTION OF AMINES ON THE REACTION OF DIPHENYLMETHANE WITH SULFUR \*

JITSUO TSURUGI

#### INTRODUCTION

The accelerating effect of amines on rubber vulcanization has been well known for a long time and studied by several workers. However, the mechanism of acceleration proposed by them has lacked experimental support. Recently, a linear relation between accelerating effects and dissociating constants of amines was found in the rubber-sulfur system<sup>1</sup> and for a rubber-sulfur-accelerator-ZnO system<sup>2</sup>.

More recently, Moore<sup>3</sup> reported on the reaction of cyclohexene (50 g) and sulfur (10 g) in the presence of diethylamine (30 g) at 140° C. The reaction mechanism is as follows.



In the presence of a considerably larger quantity of amine the mechanism was altered to an ionic one, whereas it has been shown by Farmer that sulfur alone reacts with the hydrocarbon by a radical mechanism. Furthermore, Moore could not indicate the mechanism of evolution of H<sub>2</sub>S when amine and sulfur reacted.

In the present study, diphenylmethane (DPM) which has no olefinic double bond was used as model compound of rubber hydrocarbon, so that H<sub>2</sub>S evolved could be measured. Aromatic amines were used in smaller quantities as compared with Moore's investigation. Kinetics of H<sub>2</sub>S evolution elucidated the mechanism of the accelerating effect of amine on the reaction of DPM with sulfur.

#### EXPERIMENTAL RESULTS

*Reaction products with aniline.*—DPM (200 mmoles) and sulfur (200 milligram atoms or 25 mmoles) and aniline (amounts given in Table I) were heated in a stream of nitrogen gas at 180° C for 20 hours in the same way as for Part I. H<sub>2</sub>S evolved was absorbed in iodine solution. The reaction products were distilled under vacuum. Fraction I (up to 120° C/50 mm Hg) was extracted with HCl, neutralized and again extracted with ether. This was shown to be unreacted aniline. Fraction II (up to 105° C/3 mm Hg) was treated in the same way as in Part I, and shown to contain thiobenzophenone (TBP). The distillation residues were sulfur and dibenzhydryl polysulfide (PS). The latter

\* See preceding paper, this issue, for Part II. Part III is reprinted from the *Bulletin of the University of Osaka Prefecture*, Vol. 5, Series A, pages 173-178 (1957).

TABLE I  
THE REACTION PRODUCTS OF DPM (200 MMOLES),  
 $S_8$  (25 MMOLES) AND ANILINE

Aniline, mmoles	Products in mmoles			Recovered aniline, mmoles
	H <sub>2</sub> S	PS	TBP	
0	1.2	0.81	0.30	1.11
10	5.0	2.7	0.8	3.5
25	9.0	2.3	4.0	6.3
50	9.9	2.1	4.2	6.3
				11.0

was identified and weighed as disulfide as shown in Part I. The results are tabulated in Table I.

(1) The amount of (PS + TBP) was nearly proportional to the amount of aniline up to 25 mmoles, but the quantity of products did not increase by increasing the amount of aniline above 25 mmoles.

(2) The amount of H<sub>2</sub>S increased nearly proportionally to the amount of aniline up to 25 mmoles, and in the presence of more aniline H<sub>2</sub>S increased to a lesser extent; 25 mmoles of aniline is equivalent to the sulfur used.

(3) In the absence of aniline the moles of H<sub>2</sub>S was nearly equal to that of PS plus TBP (see Part I). Table I shows that H<sub>2</sub>S is more than equivalent to PS plus TBP in the presence of aniline. This indicates that aniline itself is dehydrogenated by sulfur and evolves H<sub>2</sub>S. Results in Table I and Moore's investigation cited above support this.

*Relation between temperatures and H<sub>2</sub>S yield.*—DPM (50 mmoles), sulfur (50 milligram atoms or 6.25 mmoles) and aniline (10 mmoles) were heated in the same way as previously mentioned. H<sub>2</sub>S evolved was plotted against reaction time (Figure 1). Except for an induction period, the rate of H<sub>2</sub>S evolution ( $v$ ) was constant for the reasons considered in Part II, and is obtained, from Figure 1. The log  $v$  versus 1/T curve (Figure 2) is linear with a bend at 160° C. In the range of 160–180° C, the apparent activation energy is 9 kcal/mole.

*Effect of aniline concentration on H<sub>2</sub>S rate.*—DPM (50 mmoles), sulfur (indicated in parenthesis on Figure 3) and aniline (indicated on the abscissa for Figure 3) were heated at 160° C. Rate of H<sub>2</sub>S evolution  $v$  (mmoles/DPM,

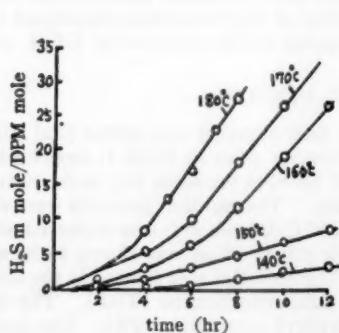


FIG. 1.—H<sub>2</sub>S and reaction time at various temperatures.

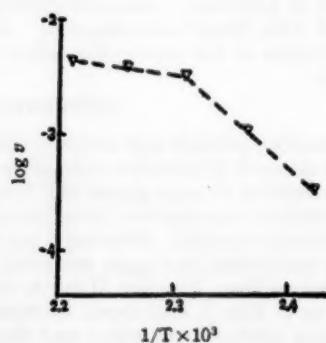


FIG. 2.—Log  $v$  versus 1/T.

moles/hr) were plotted against the aniline used. Figure 3 indicates that the rate of  $H_2S$  increases linearly with increasing amounts of aniline up to the point that aniline is equivalent to sulfur, but over this the  $H_2S$  rate increases more slowly. This result coincides with the composition of the reaction products and suggests that aniline acts upon sulfur and activates it. Figure 3 indicates further that in the range where the ratio of aniline to sulfur is less than unity, the rate of  $H_2S$  is not dependent on sulfur but on aniline. This relation holds except for the experiment at the lowest sulfur dosage and leads to

$$v \propto [\text{aniline}][\text{S}_8]^0 \quad (1)$$

*Relation between  $H_2S$  rates and dissociation constants of N-substituted amines.*—DPM (50 mmoles), sulfur (6.25 mmoles) and N-substituted aromatic amines (each 10 mmoles) were heated at 180° C and the evolution rate of  $H_2S$  ( $v$ ) were

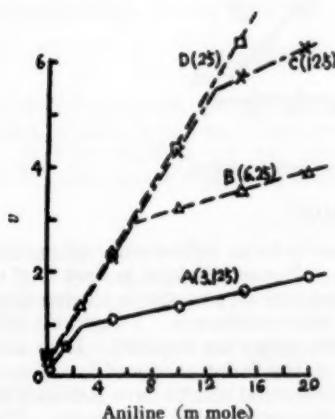


FIG. 3.— $H_2S$  rate ( $v$ ) under various sulfur and aniline concentrations.

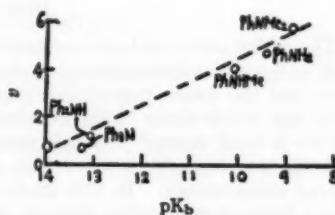


FIG. 4.— $H_2S$  rate and  $pK_b$  values.

measured, respectively. The values of  $v$  (mmoles/DPM, moles/hr) were plotted against  $pK_b$  values of amines (Figure 4). A linear relation evidently holds between  $H_2S$  rates and  $pK_b$  values.

*Relation between hydrogen sulfide rates and Hammett's  $\sigma$  constants of phenyl-substituted aromatic amines.*—The DPM (50 mmoles), sulfur (6.25 mmoles) and *p*- or *m*-substituted amines (each 10 mmoles) were heated at 180° C, and  $H_2S$  rates ( $v$ ) were measured. When aniline was used as a nonsubstituted amine under the same conditions, this rate was denoted by  $v_0$ . Log  $(v/v_0)$  were plotted against Hammett's  $\sigma$  constants (Figure 5). Except for *p*-bromoaniline this rule holds to Figure 5. This together with previous results suggests that the accelerating effect depends on the electron density on the nitrogen atom of the amine.

*Retarding action of aromatic acids.*—The preceding results have indicated that the accelerating effect of an amine depends on the electron density on the N atom due to the lone pair of electrons. If acid is added together with amine, the accelerating effect of amine will be reduced considerably. As acids, benzoic,

salicylic and phthalic acids were used, and as amines, aniline and *p*-phenylenediamine.  $H_2S$  rates were measured at 140 and 160° C. Acid and amine were used at the same concentrations as in preceding experiments. The results indicate that when acid alone is added to diphenylmethane and sulfur the rate does not alter very much and when both acid and amine are added the accelerating effect of amine is reduced considerably.

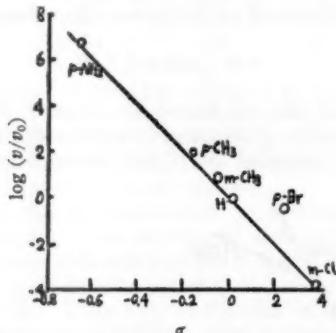
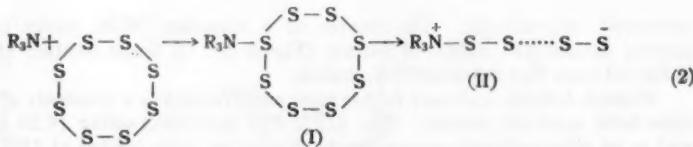


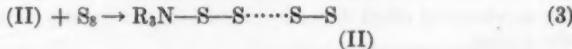
FIG. 5.— $H_2S$  rate and Hammett's  $\sigma$  constant.

#### DISCUSSION

The sulfur molecule has been considered to be an eight-membered puckered ring<sup>4</sup>, and to have some resonance energy. It was indicated in Part II of this series that the fission step of the  $S_8$  ring was rate determining in the reaction of DPM and sulfur alone in the absence of other substances. To split the sulfur ring S—S bond energy plus this resonance energy are required. If an amine forms an intermediate complex with sulfur, the fission energy of  $S_8$  ring can be reduced considerably. In this study experimental results have indicated that amines interact with sulfur through the nitrogen lone pair of electrons. Thus, the mechanism of the accelerating effect of an amine is considered as follows.

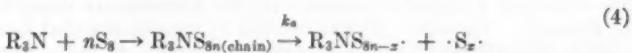


In the presence of excess sulfur molecules, (II) reacts with sulfur and lengthening of the sulfur chain occurs.



The sulfur chain of (II) splits and sets free the radical  $\cdot S_2^-$ . Since the reaction products in the presence of amine did not differ from those in the absence of amine, the radical  $\cdot S_2^-$  must be formed also in this case. From the mechanism

of fission of the  $S_8$  molecule discussed above, the rate of fission is derived as follows. Equations (2) and (3) can be modified to (4).



The succeeding steps are entirely the same as the case in the absence of amine. These are Equations (2), (3), (4), (5), (6) and (7) of Part II. In the same way as shown in Part II, the  $H_2S$  rate Equation (5) can be derived. In this equation  $k_1[S_8]$  of Equation (A) in Part II is replaced by  $k_a[R_3NS_{8n}]$ .

$$\frac{d[H_2S]}{dt} = k_a[R_3NS_{8n}]/2 + k_6(k_a/k_7)^{\frac{1}{2}}[R_3NS_{8n}]^{\frac{1}{2}} \quad (5)$$

In this paper it is considered that  $k_a$  is greater than  $k_6$  or  $k_7$ , and so the relation  $k_a/2 \gg k_6(k_a/k_7)^{\frac{1}{2}}$  can hold contrary to the lower temperature reaction of DPM and sulfur alone studied in Part II. Then (5) reduces to the simpler (6).

$$\frac{d[H_2S]}{dt} = k_a[R_3NS_{8n}]/2 \quad (6)$$

In the following discussion it is convenient to distinguish whether the ratio of amine to sulfur is less than unity or not.

(i) When  $R_3N/S_8 < 1$ , i.e., excess sulfur is present,  $[R_3NS_8]$  is equal to  $[R_3N]$ , since excess sulfur only lengthens sulfur chain of  $R_3NS_8$ . From (6),

$$\frac{d[H_2S]}{dt} = k_a[R_3N]/2 \quad (7)$$

is obtained.

(ii) When  $R_3N/S_8 > 1$ , i.e., excess amine is present, then the value of  $n$  in (4) is unity, and  $[R_3NS_8]$  is equal to  $[S_8]$ . From (6)

$$\frac{d[H_2S]}{dt} = k_a[S_8]/2 \quad (8)$$

is obtained.

The above discussion on the  $H_2S$  evolution rate refers only to the  $H_2S$  originating from DPM. Experimental results show that the amine is also dehydrogenated by sulfur to form  $H_2S$ . The rate of amine derived  $H_2S$  is denoted by  $V_{\text{amine}}$  and that from DPM is denoted by  $V_{\text{DPM}}$ . The observed  $H_2S$  rate ( $V_{\text{obs}}$ ) is the sum of  $V_{\text{DPM}}$  and  $V_{\text{amine}}$ .  $V_{\text{amine}}$  is assumed to be proportional to  $[R_3N]$ . This assumption is supported by experimental results. Then,

$$V_{\text{amine}} = k''[R_3N]$$

where  $k''$  is the proportionality constant. From this discussion

$$V_{\text{obs}} = V_{\text{DPM}} + V_{\text{amine}} = \frac{d[H_2S]}{dt} + k''[R_3N]$$

(i) When  $[R_3N]/[S_8] < 1$

$$V_{\text{obs}} = (k_a/2 + k'')[R_3N] \quad (9)$$

(ii) When  $[R_3N]/[S_8] > 1$

$$V_{\text{obs}} = k_a[S_8]/2 + k''[R_3N] \quad (10)$$

Equation (9) coincides with (1) obtained experimentally. Both (9) and (10) explain the result illustrated in Figure 3. The bend of the  $\log v$  versus  $1/T$  line in Figure 2 probably results from the temperature dependence of  $k_a$  and  $k_6, k_7$  in (5). Equation (6) was derived by considering that  $k_a$  was far greater than  $k_6$  or  $k_7$  at  $160^\circ\text{C}$  or at higher temperatures. At temperatures lower than  $160^\circ\text{C}$  another relation must hold.

#### ACKNOWLEDGMENT

The author wishes to express his thanks to Prof. N. Murata of this University, and to Prof. J. Furukawa of Kyoto University for their helpful suggestions and encouragements. Thanks are also due to Mr. T. Nakabayashi, Miss H. Fukuda and Mr. M. Uehara for their assistance in these three series of papers. These studies are being continued and a further communication will appear in the near future.

#### SYNOPSIS

The reaction products of diphenylmethane, sulfur and an aromatic amine are hydrogen sulfide, benzhydryl polysulfide and thiobenzophenone. The amine is also attacked by sulfur and evolves hydrogen sulfide. Hydrogen sulfide evolved during the reaction was determined at various temperatures and at various aniline concentrations. All of the experimental results indicate that aniline attacks the S<sub>8</sub> ring molecule initially. Determinations of hydrogen sulfide formation rate with various N-substituted aromatic amines and with various phenyl-substituted anilines indicate that the accelerating effect depends on electron density conferred by the lone electron pair on the N atom of the amine.

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## IV. ACTION OF 2-MERCAPTOBENZOTHIAZOLE ON THE REACTION OF DIPHENYLMETHANE AND SULFUR \*

JITSUO TSURUGI AND TAKESHIGE NAKABAYASHI

### INTRODUCTION

In Part I<sup>1</sup> of this series, the mechanism of the reaction of diphenylmethane (DPM) and sulfur was discussed, and in Part II<sup>2</sup>, a kinetic investigation was carried out. In this paper, the mechanism and kinetics of the reaction involving DPM, sulfur and 2-mercaptopbenzothiazole (MBT) will be reported and compared with those of Parts I and II, respectively. Thus the accelerating effect of MBT has been elucidated clearly. DPM which has no olefinic double bonds but which has  $\alpha$ -methylene hydrogen adjacent to aromatic double bonds has been shown to be an excellent model for studying the mechanism of acceleration by the methods of organic chemistry. The significance of DPM as a model of rubber hydrocarbon in the presence of sulfur alone was discussed in Part I. British investigators<sup>3</sup> using olefins such as dihydromyrcene and squalene as models studied the mechanism of acceleration. However, they could not deduce the mechanism so clearly as we in this paper, only because the reaction of olefins with sulfur seemed to be more complex than that of DPM.

Investigations on the reaction of DPM, sulfur and accelerators in the presence of either zinc oxide or zinc soap will be reported in other papers of this series.

### EXPERIMENTAL

Materials other than accelerators, the procedure to carry out the reaction, and the method of determining hydrogen sulfide evolved during the reaction already have been reported in Part I<sup>1</sup>. Commercial MBT was recrystallized several times to constant melting point (178° C). 2-Mercaptobenzoxazole<sup>4</sup>, 2-mercaptopbenzimidazole<sup>4</sup> and diphenylthiourea<sup>5</sup>, also used as accelerators in this study, were prepared by methods described in the literature. 2-Oxobenzothiazole was prepared by oxidizing 2-mercaptopbenzothiazole with hydrogen peroxide.

After a given reaction time the reaction system was cooled. Brown red crystals which were precipitated from the reaction mass were filtered by suction. The filtrate contained DPM, thiobenzophenone (TBP) and benzhydryl polysulfide (PS). The identification and determination of the latter two compounds were reported in Part I. The brown red crystals were dissolved in benzene and the solution shaken with aqueous basic lead acetate solution. The yellow lead mercaptide of 2-mercaptopbenzothiazole precipitated in the benzene layer. A brown red color remained in benzene, and after evaporation of solvent a brown red oily substance remained which could not be identified because of the small quantity.

\* See preceding paper, this issue, for Part III. Part IV is reprinted from the *Bulletin of the University of Osaka Prefecture*, Vol. 5, Series A, pages 135-143 (1958).

## RESULTS AND DISCUSSION

*Stoichiometric relations.*—The reaction products are indicated in Table I. The following relations are permitted by the data in Table I.

(1) Within experimental error, the amount of hydrogen sulfide is nearly equal to the sum of PS and TBP. This relation also holds for the reaction of DPM and sulfur alone. (See Part I.)

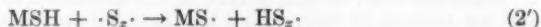
(2) The amount of MBT started with does not differ from that of MBT recovered within the experimental error. The MBT used is recovered quantitatively.

(3) The accelerating effect measured by hydrogen sulfide evolution increases with an increasing amount of starting MBT at lower concentrations, but becomes constant at the higher concentrations of MBT.

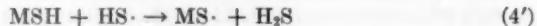
TABLE I  
THE REACTION PRODUCTS OF DPM (200 MMOLIES), SULFUR (40 MILLIGRAM ATOMS) AND MBT AT 160° C, 20 HOURS

No.	MBT used (mmole)	Products (mmoles)				(PS + TBP) (mmoles)
		H <sub>2</sub> S	TBP	PS	MBT	
1	20	1.20	0.343	0.723	18.55	1.086
2	10	1.191	0.328	0.701	8.94	1.029
3	5	1.100	0.278	0.639	3.62	0.917
4	2.5	0.886	0.171	0.529	1.67	0.700
5	1.25	0.636	—	—	—	—
6	0.625	0.430	—	—	—	—
7	0	0.246	—	—	—	—

*Mechanism of acceleration.*—The stoichiometric relations (1) and (2) are understandable if one assumes that MBT acts as a hydrogen carrier<sup>6,7</sup>. MBT is dehydrogenated by the sulfur radical and yields the mercaptobenzothiazolyl radical. This radical dehydrogenates DPM and returns to MBT again, yielding the diphenylmethyl radical. If MBT is denoted by MSH, the reaction sequence mentioned above can be indicated as follows.



The radical HS<sub>2</sub><sup>·</sup> in (2') gives the radical HS<sup>·</sup> as shown by (3) in Part II, and this radical attacks MBT as follows.



Summing (2') and (4''), (2) of Part II is obtained.



Adding (4') to (4''), (4) of Part II is obtained.



The stoichiometric relations (1) and (2) of the preceding section are understandable from this discussion. (Also see Parts I and II.)

It has been concluded in Parts I and II that the fission step of the  $S_8$  ring is rate determining. If MBT took part in the reaction only as hydrogen carrier as mentioned above, and therefore, if MBT did not contribute to the rate determining step, the reaction could not be accelerated by MBT. Experimental results, however, indicate its accelerating effect. Therefore, it is necessary to consider the steps in which the radical  $MS\cdot$  splits the  $S_8$  ring and gives the radical  $\cdot S_x\cdot$  as follows.



It has been reported by other investigators<sup>8,9</sup> that radicals generated from accelerators attack and split the  $S_8$  ring.

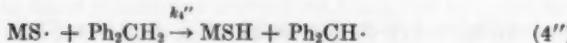
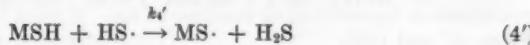
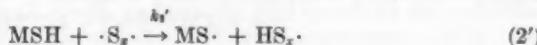
*Kinetics of hydrogen sulfide evolution.*—From the above discussion, the rate equation for hydrogen sulfide evolution accelerated by MBT can be derived. Table I indicates that even in the absence of MBT some  $H_2S$  was evolved. This amount of  $H_2S$ , of course, results from the reaction of DPM and sulfur alone as described in Parts I and II. In this paper the rate of hydrogen sulfide evolution due to Reactions (2), (3) and (4) of Part II is denoted by  $V_{DPM}$  and that due to Reactions (2'), (3) and (4') by  $V_{MSH}$ . If the observed rate is denoted by  $V_{obs}$ ,

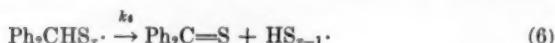
$$V_{obs} = V_{DPM} + V_{MSH}$$

At very small concentration of MBT, Reaction (2) of Part II predominates over Reaction (2'), and (4) of Part II over (4'). In this case  $V_{DPM}$  cannot be neglected as compared with  $V_{MSH}$ . On the contrary, at large concentration of MBT, the opposite relation holds. Then  $V_{DPM}$  is neglected and  $V_{obs}$  is equal to  $V_{MSH}$ .

Since it is not MBT but its radical  $MS\cdot$  that splits the  $S_8$  ring, the fission of the  $S_8$  ring is the essential initiation step. As stated above, under small MBT concentrations (2') does not occur smoothly only for the reason that the concentration of MBT is small. Therefore, in order to derive  $V_{MSH}$  at all MBT concentrations, especially at low concentrations, the equilibrium state must be the reversible fission of  $S_8$  rings as shown in (1), in spite of the fact that this step is rate determining.

The succeeding steps in which MBT takes part were mentioned in the preceding section, and the steps necessary for hydrogen sulfide evolution were given in Part II. The latter are (5), (6) and (7) below. All of these are indicated below for the sake of convenience.





It is particularly gratifying to find that when  $\text{Ph}_2\text{CH}_2$  is replaced by RH these equations except for (6) are valid for all hydrocarbons which have an  $\alpha$ -methylene group. Hence, it is concluded that the mechanism of acceleration may be indicated by these equations. Equation (6) is the decomposition step for the radical  $\text{Ph}_2\text{CHS}_{x\cdot}$ , and this step may differ as the structure of original hydrocarbon differs.

The hydrogen sulfide evolution rate derived from this reaction sequence should be  $V_{\text{MSH}}$ . Applying the stationary state method the following relations are obtained.

$$d[\cdot \text{S}_{x\cdot}] / dt = k_1[\text{S}_8] - k_1'[\cdot \text{S}_{x\cdot}] - k_2'[\text{MSH}][\cdot \text{S}_{x\cdot}] + k_3[\text{HS}_{x\cdot}] + k_1[\text{MSS}_8\cdot] - k_5[\text{Ph}_2\text{CH}\cdot][\cdot \text{S}_{x\cdot}] = 0 \quad (i)$$

$$d[\text{Ph}_2\text{CH}\cdot] / dt = k_4''[\text{MS}\cdot][\text{Ph}_2\text{CH}_2] - k_5[\text{Ph}_2\text{CH}\cdot][\text{S}_{x\cdot}] = 0 \quad (ii)$$

$$d[\text{Ph}_2\text{CHS}_{x\cdot}] / dt = k_5[\text{Ph}_2\text{CH}\cdot][\cdot \text{S}_{x\cdot}] - k_6[\text{Ph}_2\text{CHS}_{x\cdot}] - k_7[\text{Ph}_2\text{CHS}_{x\cdot}]^2 = 0 \quad (iii)$$

$$d[\text{HS}_{x\cdot}] / dt = k_2'[\text{MSH}][\cdot \text{S}_{x\cdot}] - k_3[\text{HS}_{x\cdot}] + k_6[\text{Ph}_2\text{CHS}_{x\cdot}] = 0 \quad (iv)$$

$$d[\text{HS}\cdot] / dt = k_3[\text{HS}_{x\cdot}] - k_4'[\text{MSH}][\text{HS}\cdot] = 0 \quad (v)$$

$$d[\text{MS}\cdot] / dt = k_2'[\text{MSH}][\cdot \text{S}_{x\cdot}] + k_4'[\text{MSH}][\text{HS}\cdot] - k_4''[\text{MS}\cdot][\text{Ph}_2\text{CH}_2] - k_{11}[\text{MS}\cdot][\text{S}_8] + k_{12}[\text{MSS}_8\cdot] = 0 \quad (vi)$$

$$d[\text{MSS}_8\cdot] / dt = k_{11}[\text{MS}\cdot][\text{S}_8] - k_{12}[\text{MSS}_8\cdot] = 0 \quad (vii)$$

If the relations (ii), (v) and (vii) are put in (i), (iii) and (vi), the following relations are obtained.

$$k_1[\text{S}_8] - k_1'[\cdot \text{S}_{x\cdot}] - k_2'[\text{MSH}][\cdot \text{S}_{x\cdot}] + k_3[\text{HS}_{x\cdot}] + k_{11}[\text{MS}\cdot][\text{S}_8] - k_4''[\text{MS}\cdot][\text{Ph}_2\text{CH}_2] = 0 \quad (i)'$$

$$k_4''[\text{MS}\cdot][\text{Ph}_2\text{CH}_2] - k_6[\text{Ph}_2\text{CHS}_{x\cdot}] - k_7[\text{Ph}_2\text{CHS}_{x\cdot}]^2 = 0 \quad (iii)'$$

$$k_2'[\text{MSH}][\cdot \text{S}_{x\cdot}] + k_3[\text{HS}_{x\cdot}] - k_4'[\text{MS}\cdot][\text{Ph}_2\text{CH}_2] = 0 \quad (vi)'$$

From (i)' and (vi)',

$$k_1[\text{S}_8] - k_1'[\cdot \text{S}_{x\cdot}] - 2k_2'[\text{MSH}][\cdot \text{S}_{x\cdot}] + k_{11}[\text{MS}\cdot][\text{S}_8] = 0. \quad (viii)$$

At a stationary state, the following relation is assumed to hold.

$$k_1[\text{S}_8] = m k_{11}[\text{MS}\cdot][\text{S}_8] \quad (14)$$

This assumption is essential to derive the  $\text{H}_2\text{S}$  rate equation, and will be discussed in detail in the next section. From (14) and (viii),

$$[\cdot\text{S}_x\cdot] = \frac{1+m}{m} \cdot \frac{k_1[\text{S}_8]}{k_1' + 2k_2'[\text{MSH}]}$$

From (iv), (vi)' and (iii)',

$$[\text{Ph}_2\text{CHS}_x\cdot] = \left( \frac{1+m}{m} \cdot \frac{2k_1k_2'[\text{MSH}][\text{S}_8]}{k_7(k_1' + 2k_2'[\text{MSH}])} \right)^{\frac{1}{2}}$$

The rate equation can be derived as follows.

$$\begin{aligned} V_{\text{MSH}} &= d[\text{H}_2\text{S}]/dt = k_4'[\text{MSH}][\text{HS}\cdot] = k_3[\text{HS}_x\cdot] \\ &= k_2'[\text{MSH}][\cdot\text{S}_x\cdot] + k_6[\text{Ph}_2\text{CHS}_x\cdot] \\ &= \frac{1+m}{m} \cdot \frac{k_1k_2'[\text{MSH}][\text{S}_8]}{k_1' + 2k_2'[\text{MSH}]} \\ &\quad + k_6 \left( \frac{1+m}{m} \cdot \frac{2k_1k_2'}{k_7} \cdot \frac{[\text{MSH}][\text{S}_8]}{k_1' + 2k_2'[\text{MSH}]} \right)^{\frac{1}{2}} \end{aligned} \quad (15)$$

Since the step (1) is rate determining at lower temperatures,  $k_1$  is far smaller than  $k_2'$ ,  $k_6$  or  $k_7$ . The first term of (15) can be neglected as compared with the second term at lower temperatures. Then,

$$V_{\text{MSH}} = k_6 \left( \frac{1+m}{m} \cdot \frac{2k_1k_2'}{k_7} \cdot \frac{[\text{MSH}][\text{S}_8]}{k_1' + 2k_2'[\text{MSH}]} \right)^{\frac{1}{2}} \quad (16)$$

At very small concentrations of MBT,  $k_1' \gg 2k_2'[\text{MSH}]$ , then (16) reduces to (17).

$$V_{\text{MSH}} = \left( \frac{1+m}{m} \right)^{\frac{1}{2}} k_6 \left( \frac{2k_1k_2'}{k_1'k_7} \right)^{\frac{1}{2}} [\text{MSH}]^{\frac{1}{2}} [\text{S}_8]^{\frac{1}{2}} \quad (17)$$

At very large concentrations of MBT,  $k_1' \ll 2k_2'[\text{MSH}]$ , then (16) reduces to (18).

$$V_{\text{MSH}} = (1+m)^{\frac{1}{2}} m^{-\frac{1}{2}} k_6 k_1' k_7^{-\frac{1}{2}} [\text{S}_8]^{\frac{1}{2}} \quad (18)$$

*Determination of hydrogen sulfide.*—Figures 1a and 1b show the hydrogen sulfide versus reaction time curves, and indicate that except for the induction period, the values of  $V_{\text{obs}}$  are constant. In these experiments DPM (100 mmoles), sulfur (20 milligram atoms) and MBT (5 mmoles) were used, and under this concentration of MBT,  $V_{\text{obs}}$  is equal to  $V_{\text{MSH}}$  as previously mentioned. The constant value of  $V_{\text{MSH}}$  is interpreted by (16) or (18) as follows. Since  $[\text{MSH}]$  is constant and  $[\text{S}_8]$  can be assumed to be constant as mentioned in Part II,  $V_{\text{MSH}}$  should be constant.

Figure 2 shows the linear relationship between  $\log V_{\text{MSH}}$  and  $1/T$ , and apparent activation energy of 27.5 kcal. The values of  $V_{\text{obs}}$  at various constant

sulfur concentrations (12.5, 25, 50 mmoles per mole DPM, respectively) were plotted against MBT used (mmoles per mole DPM) in Figure 3. The determination of hydrogen sulfide was conducted at 160° C. Figure 3 indicates that at very small concentration of MBT, the values of  $V_{obs}$  increase with increasing amounts of MBT. This result is interpreted by (17). On the other hand, at very large concentrations of MBT the values of  $V_{obs}$  do not depend on the MBT concentrations but on those of sulfur. The values of  $V_{obs}$  approach the

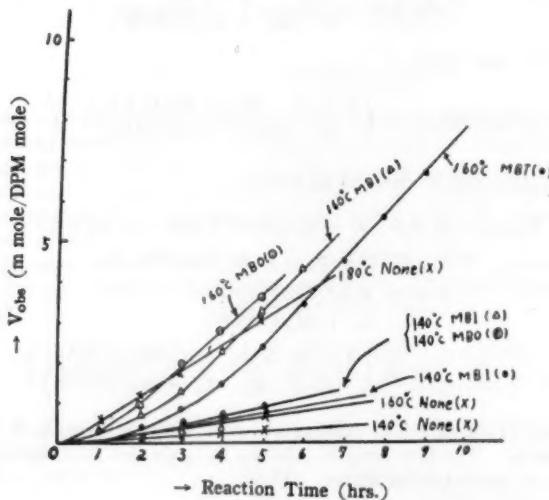


FIG. 1a.

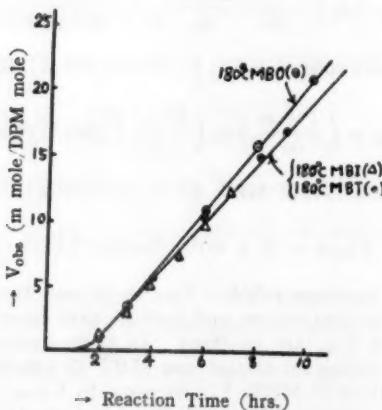


FIG. 1b.

FIG. 1a and FIG. 1b.— $V_{obs}$  versus reaction time curves.  
 MBT: 2-mercaptopbenzothiazole      MBO: 2-mercaptopbenzoxazole  
 MBI: 2-mercaptopbenzimidazole      None: No accelerator  
 Recipe: DPM (100 mmoles), sulfur (20 milligram atoms) and  
 accelerator (5 mmoles).

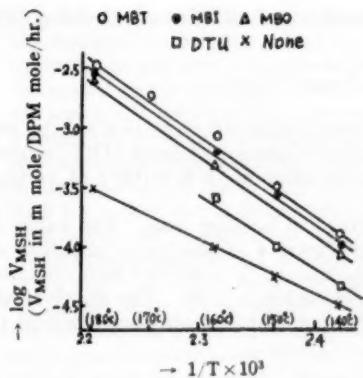


FIG. 2.— $\log V_{\text{MSH}}$  versus  $1/T$  curves.  
Recipe is the same as Figure 1. DTU: di-phenylthiourea.

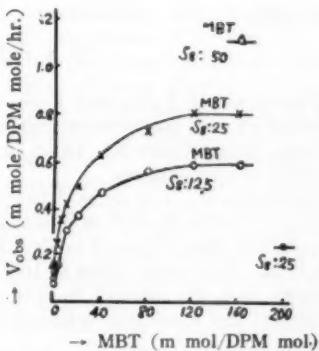


FIG. 3.—Relation between  $V_{\text{obs}}$  and MBT concentrations at  $160^{\circ}\text{C}$ .  $S_8$  concentrations are indicated in mmoles/DPM mole.

limiting values under a given sulfur concentration. In Figure 4 these limiting values of  $V_{\text{obs}}$  ( $= V_{\text{MSH}}$ ) were plotted against sulfur concentrations both in log scale. Figure 4 shows that the relation

$$\log V_{\text{MSH}} = \text{const.} + (1/2) \log [S_8] \quad (19)$$

holds. Equation (19) coincides with (18) completely.

The constant  $m$  in (14) will now be discussed. As previously reported in Part II,  $V_{\text{DPM}}$ , i.e., the hydrogen sulfide rate for the reaction between DPM and sulfur alone, is given by (20) at lower temperatures.

$$V_{\text{DPM}} = k_6(k_1/k_7)^{1/2}[S_8]^{1/2} \quad (20)$$

If the radical  $\text{MS}^{\cdot}$  would not split the  $S_8$  ring, that is, (11) and (12) would be omitted from the overall reaction sequence, the  $V_{\text{MSH}}$  calculated is the same as (20). On the contrary when (11) and (12) take part in the reaction sequence (14) becomes essential in order to calculate the rate equation. From (14) the constant  $m$  signifies the ratio of  $S_8$  ring fission by mercaptobenzothiazolyl radicals to thermal and spontaneous fission, and should be defined as the acceleration coefficient of mercaptan type accelerators.

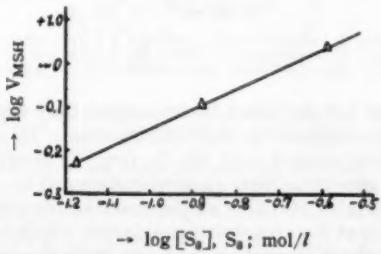


FIG. 4.—Relation between  $\log V_{\text{MSH}}$  and  $\log [S_8]$  at  $160^{\circ}\text{C}$ .  
 $V_{\text{MSH}}$  in mmole/DPM moles/hr.

The experimental values of  $m$  can be obtained as follows. Dividing (18) by (20),

$$(1 + m)^{\frac{1}{2}}m^{-\frac{1}{2}} = V_{MSH}/V_{DPM}.$$

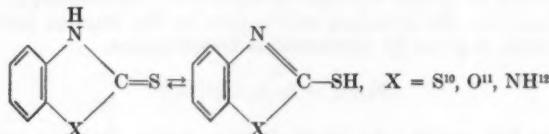
The values of  $V_{MSH}$  and  $V_{DPM}$  at the same sulfur concentration can be obtained at very large concentration and at zero concentration of MBT, respectively, from Figure 3. Table II shows the value of  $(1 + m)^{\frac{1}{2}}m^{-\frac{1}{2}}$  at various sulfur concentrations.

The value of  $(1 + m)^{\frac{1}{2}}m^{-\frac{1}{2}}$  can be obtained in another way. The value of  $(1 + m)^{\frac{1}{2}}m^{-\frac{1}{2}}k_6(k_1/k_7)^{\frac{1}{2}}$  is evaluated from Figure 4 of this paper and that of  $k_6(k_1/k_7)^{\frac{1}{2}}$  from Figure 2 in Part II. The value of  $(1 + m)^{\frac{1}{2}}m^{-\frac{1}{2}}$  thus obtained is 6.65. The mean value at 160° C is 6.68, and  $m$  is 1/45. The above result shows that the ratio of  $S_8$  ring fission by mercaptobenzothiazolyl radical to thermal and spontaneous fission is 45.

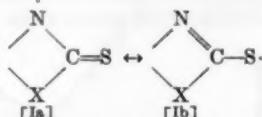
TABLE II  
 $(1 + m)^{\frac{1}{2}}m^{-\frac{1}{2}}$  VALUES CALCULATED FROM FIGURE 3

$[S_8]$ in mmoles/mole DPM	12.5	25	50
$(1 + m)^{\frac{1}{2}}m^{-\frac{1}{2}}$	7.05	6.7	6.75

*Relation between accelerating effect and structure of accelerators.*—Figure 2 shows that 2-mercaptobenzoxazole, 2-mercaptobenzimidazole and diphenylthiourea as well as MBT have an accelerating effect and that their accelerating mechanisms are alike. The three mercaptobenzazole compounds exhibit a similar tautomerism as indicated below.



Diphenylthiourea also exhibits a similar tautomerism. The radicals which are formed when accelerators are dehydrogenated by sulfur radicals may be stabilized by resonance as follows.



If these radicals were not stabilized by resonance, they would return readily to mercaptans by dehydrogenating the hydrocarbon. In this case, only (4'') occurs and the radical cannot split the  $S_8$  ring. Therefore, it must be concluded that radicals generated from an accelerator must have a proper resonance energy and a considerable stability at the reaction temperature.

It is well known that 2-mercaptobenzimidazole, which is assumed to be more stabilized than the others, cannot be used as a vulcanization accelerator but is used as an antioxidant in the rubber industry. It might be considered that

this fact contradicts the experimental results indicated in Figure 2. However, the reaction is conducted under an inert gas atmosphere in this study, on the contrary, in industry, the processing is in an atmosphere of oxygen. It was recognized also in this paper that hydrogen sulfide evolution was inhibited when air was mixed with the inert gas stream. This inhibitory effect by air is the greater, the lower the reaction temperature. Also in the presence of MBT the hydrogen sulfide evolution was inhibited by air but to a lesser extent than with 2-mercaptopbenzimidazole. In the case of the presence of air, it is assumed that the accelerator is dehydrogenated by oxygen molecules to form radicals. It is considered that a radical stabilized excessively by resonance, for instance, 2-mercaptopbenzimidazolyl radical, can neither return to mercaptan nor split the S<sub>8</sub> ring. It couples readily to other radicals and loses any accelerating effect.

In this paper it was verified by determining hydrogen sulfide evolution that the compounds which have substituents such as benzhydryl attached to mercapto groups and thiazole derivatives, such as 2-amino- or 2-oxobenzothiazole, have no accelerating effect. These compounds cannot give an effective radical such as [I]. It has been reported by other investigators that thiazole derivatives such as 4,5-dimethyl-2-mercaptopthiazole<sup>13</sup> or 2-mercaptopnaphthothiazole<sup>14</sup> have accelerating properties in rubber vulcanization. These compounds would give effective radicals similar to [I]. Therefore, it is necessary for accelerator to give an effective radical such as [I]. The thiazole group is not necessarily indispensable for acceleration.

### SYNOPSIS

Diphenylmethane was used as a model of rubber hydrocarbon, and the reaction involving diphenylmethane, sulfur and 2-mercaptopbenzothiazole (accelerator) in the absence of zinc oxide was investigated. The reaction products derived from diphenylmethane were hydrogen sulfide, benzhydryl polysulfide and thiobenzophenone and did not differ from those in the absence of the accelerator, but their amounts increased in the presence of the accelerator. 2-Mercaptopbenzothiazole itself was recovered quantitatively from the reaction mass. The same stoichiometric relation held in the presence as absence of the accelerator. It was concluded that the accelerating mechanism consisted of the mercaptobenzothiazolyl radical splitting the S<sub>8</sub> ring and setting free sulfur radicals. A reaction mechanism and rate equations are discussed which interpret all the experimentally determined rates of hydrogen sulfide formation. The relation between the structures and the accelerating effects of mercapto-type accelerators is discussed and the acceleration coefficient *m* defined.

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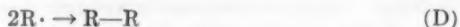
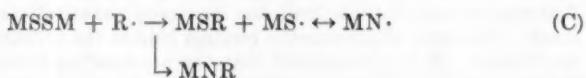
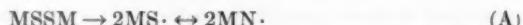
## V. ACTION OF 2,2'-BENZOTHIAZOLYL DISULFIDE ON THE REACTION OF DIPHENYLMETHANE AND SULFUR \*

JITSUO TSURUGI AND HARUKO FUKUDA

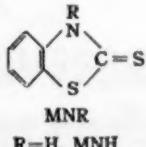
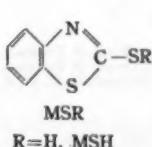
### INTRODUCTION

In Part IV, the mechanism and kinetics of the reaction involving 2-mercaptopbenzothiazole (MBT), diphenylmethane (DPM) and sulfur were discussed. In this paper, the action of 2,2'-benzothiazolyl disulfide (MBTS) on the reaction of DPM and sulfur will be discussed. The stoichiometric relations among the products, accelerating mechanism and kinetics were compared with those of Part IV. It was found that DPM is an excellent model in studying the mechanism of acceleration.

The reaction between DPM and MBTS in the absence of sulfur has been already reported by the authors<sup>1</sup>. The similar reaction between MBTS and olefins such as cyclohexene has been also investigated by a British investigator<sup>2</sup> who proposed a similar reaction mechanism to that proposed by the authors. If hydrocarbon is denoted by RH, and MBTS by MSSM, the reaction sequence is as follows.



Symbols MSH, MSR and MNH, MNR are illustrated below.



The tautomerism ( $\text{MSH} \rightleftharpoons \text{MNH}$ ) and resonance ( $\text{MS}\cdot \leftrightarrow \text{MN}\cdot$ ) have been already discussed in Part IV. The reaction steps (A) and (B) will contribute to the elucidation of mechanism of the reaction of DPM with sulfur and MBTS.

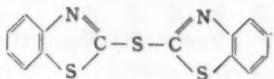
\* See preceding paper, this issue for Part IV. Part V is reprinted from the *Bulletin of the University of Oeako Prefecture*, Vol. 6, Series A, pages 145-154 (1958).

## EXPERIMENTAL

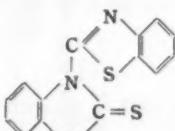
*Identification and determination of the products.*—DPM, sulfur and MBTS were heated in the inert gas stream. Hydrogen sulfide evolved during the reaction was swept out from the flask and absorbed in iodine solution. Detailed analytical procedures for hydrogen sulfide were reported in Part I<sup>3</sup> of this series. After a given time the reaction system was cooled. The crystallized product was found to be MBT, whose identification and determination were reported in Part IV. The filtrate was distilled under 4 mm Hg. DPM and thiobenzophenone (TBP) were obtained. Identification and determination of the latter were also reported in Part I. Distillation residues were dissolved in benzene and chromatographed through an alumina column. The effluent was divided into the following fractions according to color.

1. A colorless effluent crystallized to give a mixture of *sym*-tetraphenylethane and tetraphenylethylene after distilling off the solvent. This was proved by ultraviolet absorption spectra.

2. A blue effluent contained a small amount of TBP and DPM, which remained in the distilling flask after removing the solvent. The blue color resulted from TBP. Besides these substances the effluent contained MSCHPh<sub>2</sub> and a small amount of MSM and MNM. Symbols MSM and MNM are illustrated as follows.



MSM



MNM

An isomeric mixture (MSCHPh<sub>2</sub> and MNCHPh<sub>2</sub>) was isolated from another mixture (MSM and MNM) by recrystallization.

3. A pale green effluent crystallized to give a mixture of MSM and MNM. Besides these compounds a small amount of MSCHPh<sub>2</sub> was obtained. An isomeric mixture (MSM and MNM) was separated from MSCHPh<sub>2</sub> by recrystallization. Synthesis, identification and properties of individual compounds (MSCHPh<sub>2</sub>, MNCHPh<sub>2</sub>, MSM and MNM) and the method of separating one isomer from another have been reported in another paper<sup>1</sup>. In this paper, however, only the mixture of isomers was determined, since amounts of individuals were not important to the following discussion.

4. A brown effluent gave a brown oily substance after filtering off a mixture of MSM and MNM crystals. This oily substance was digested in acetone saturated with aqueous Na<sub>2</sub>SO<sub>3</sub> and converted to benzhydryl disulfide. The oily substance was found to be benzhydryl polysulfide (PS). The detailed procedure has been reported in Part I<sup>3</sup>.

*For kinetic studies.*—DPM (0.5 mole), sulfur and MBTS were heated in a four-necked flask in the stream of inert gas under mechanical stirring. About 1 g of the contents was pipetted from time to time without interrupting the reaction and analyzed for MBT. Hydrogen sulfide evolved during the reaction was determined as well. For this determination the reaction mixture was heated in a ground jointed three-necked flask. Hydrogen sulfide swept out by a gas stream was absorbed in iodine solution. This solution was exchanged for a new one at regular time intervals and titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution.

TABLE I  
THE REACTION PRODUCTS OF DPM (200 MMOL). SULFUR AND MBTS

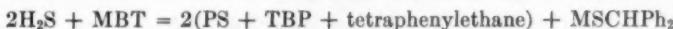
Experimental conditions		Products (mmoles)										Recovery, %	
		Temp. (° C.)	Hours (hrs)	MBTS (mmoles)	S (milli- gram atoms)	Unreacted MBTS (mmoles)	PS	TBP	TP- Ethane	TP- Ethy- lene	MSCHPh <sub>3</sub>	MSM + MNMM	MBT
1	160	20	10	40	0.24	5.0 <sub>b</sub>	0.42	0.45	0.40	0.66	15.0	83.6	79
2	160	20	5	40	0.42	2.8 <sub>2</sub>	0.40	0.80	—	—	8.14	81.4	89.5
3	160	10	5	40	0.07 <sub>6</sub>	3.3	0.35	—	—	—	9.04	90.4	79.5
4	160	20	10	80	0.31	7.1 <sub>2</sub>	0.33	—	0.15	0.13	17.4	89.1	79
5	140	20	5	40	1.05	0.03 <sub>6</sub>	1.9	0.65	—	—	7.2	93	71

## RESULTS AND DISCUSSION

**Reaction products.**—Table I shows the reaction products together with reaction conditions. Calculation of material balance from Table I serves to examine the accuracy of the experiment. MBTS used was converted to MBT, MSCHPh<sub>2</sub> and MSM, where MSCHPh<sub>2</sub> and MSM represented another isomer, respectively, for the sake of brevity. Since both MBTS and MSM contain two benzothiazolyl groups the percentage recovery of

$$\text{MBT} = \frac{\text{MBT} + \text{MSCHPh}_2 + 2\text{MSM} + 2(\text{unreacted MBTS})}{2(\text{MBTS used})} \times 100$$

The balance of hydrogen atoms is as follows. Hydrogen sulfide and MBT resulted from dehydrogenation of DPM, and at the same time, DPM gave PS, TBP, tetraphenyl-ethane, -ethylene and MSCHPh<sub>2</sub>. Since the amounts of both tetraphenyl-ethane and -ethylene are relatively small, tetraphenylethane may represent the ethylene in the following relation.



Since the products which appear in the left side of this equation can be determined more simply than those in the right side, the accuracy for determining the latter may be ascertained by the following equation.

Percentage recovery of hydrogen

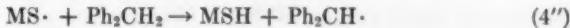
$$= \frac{2(\text{PS} + \text{TBP} + \text{tetraphenylethane}) + \text{MSCHPh}_2}{2\text{H}_2\text{S} + \text{MBT}} \times 100$$

Table I indicates that these values are satisfactory regardless of the complex nature of the reaction.

**Mechanism.**—In experiments 1 and 4 a relatively large amount of MBTS was used, and then a mixture of tetraphenyl-ethane, -ethylene and isomeric mixtures (MSCHPh<sub>2</sub> and MNCHPh<sub>2</sub>), (MSM and MNM) was formed. The mechanism for the formation of tetraphenylethane and an isomeric mixture (MSCHPh<sub>2</sub> and MNCHPh<sub>2</sub>) has been stated before. (See (C) and (D).) The fact that the formation of isomeric mixture (MSM and MNM) is attributable to decomposition of MSCHPh<sub>2</sub>, and the mechanism of formation of tetraphenylethyne have been shown elsewhere<sup>1</sup> by the authors. When the amount of MBTS used is relatively small, the direct interaction between DPM and MBTS is suppressed. Then the products become simple, and coincide with those from the reaction involving DPM, sulfur and MBT as well as those from the reaction between DPM and sulfur alone. (See Parts I and IV.) The following discussion will be limited to the point of view of model experiments of rubber vulcanization.

It is advantageous to compare the results of Table I with those of the previous paper in order to deduce the reaction mechanism.

1. MBTS was converted to MBT as the reaction proceeded. When MBTS is denoted by MSSM, the initial step is indicated by (10), and the formation of MBT by (4'').



These equations have been already cited as (A) and (B), respectively, in which tautomerism ( $\text{MSH} \rightleftharpoons \text{MNH}$ ) and resonance ( $\text{MS}\cdot \leftrightarrow \text{MN}\cdot$ ) were discussed. For the studies of mechanism and kinetics the elementary reaction steps may be simplified as in (10) and (4'').

2. The relation  $\text{H}_2\text{S} < (\text{PS} + \text{TBP})$  holds in this paper, while in the reaction involving DPM, sulfur and MBT as well as between DPM and sulfur alone, the relation  $\text{H}_2\text{S} = (\text{PS} + \text{TBP})$  holds. The difference can be interpreted as follows. When MBT is used as accelerator in the reaction, it remained after the reaction. How MBT evolved hydrogen sulfide during the reaction was indicated in Part IV. How MBTS was converted to MBT is already indicated by (10) and (4''). Hydrogen sulfide evolves only when MBT is produced from MBTS. Therefore, the relation  $\text{H}_2\text{S} < (\text{PS} + \text{TBP})$  holds in the presence of MBTS, and the amount of hydrogen sulfide increases with the increasing reaction time and, on the other hand, decreases with the increasing amount of MBTS as indicated in Table I. From the point of view of hydrogen abstraction from DPM, MSH in (4'') corresponds to  $(1/2)\cdot\text{H}_2\text{S}$ . The simplified equation of percentage recovery of hydrogen,



is readily understood on this basis.

3. In the presence of MBTS, the amount of  $(\text{PS} + \text{TBP})$  is far greater than in the presence of MBT, and increases with increasing amount of MBTS. On the other hand, it has been reported in Part IV that MBT has its upper limit of accelerating efficiency regardless of its concentration. This difference is interpreted as follows. The accelerating effect consists in the following steps, in which radicals produced from the accelerator split  $\text{S}_8$  ring molecules.



Adding the above two equations,



In the case of MBT, the formation of the radical  $\cdot\text{S}_x\cdot$  is essential in order to generate the radical  $\text{MS}\cdot$  from MBT as indicated below.



Since the radical  $\cdot\text{S}_x\cdot$  is formed by the thermal and spontaneous decomposition of the  $\text{S}_8$  molecule, an accelerating efficiency of MBT at high concentration does not depend on its concentration but on sulfur concentration. Since the formation of the radical  $\text{MS}\cdot$  depends on (10) in the case of MBTS, the accelerating efficiency of MBTS increases with increasing concentration. The radical  $\cdot\text{S}_x\cdot$  formed as indicated in (11) may induce the decomposition of MBTS as follows.

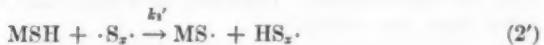
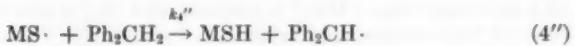
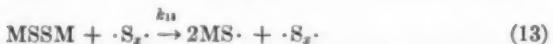


Adding the above two equations,



Whether this induced decomposition occurs in the reaction sequence or not will be decided in the following sections.

*Kinetics.*—All of the elementary reaction steps are indicated below for the convenience of calculation. Equations (3), (4'), (5), (6) and (7) have been already cited and thoroughly discussed in a previous Part.



It is gratifying in this case also to find that these equations except for (6) are valid for all the hydrocarbons which have an  $\alpha$ -methylene group.

Applying the stationary state method, the following relations are obtained.

$$d[\cdot\text{S}_x \cdot]/dt = k_{11}[\text{MS} \cdot][\text{S}_8] - k_2'[\text{MSH}][\cdot\text{S}_x \cdot] + k_3[\text{HS}_x \cdot] - k_5[\text{Ph}_2\text{CH} \cdot][\cdot\text{S}_x \cdot] = 0 \quad (i)$$

$$d[\text{MS} \cdot]/dt = 2k_{10}[\text{MSSM}] + 2k_{13}[\text{MSSM}][\cdot\text{S}_x \cdot] - k_4''[\text{MS} \cdot][\text{Ph}_2\text{CH}_2] + k_2'[\text{MSH}][\cdot\text{S}_x \cdot] + k_4'[\text{MSH}][\text{HS} \cdot] = 0 \quad (ii)$$

$$d[\text{Ph}_2\text{CH} \cdot]/dt = k_4''[\text{MS} \cdot][\text{Ph}_2\text{CH}_2] - k_5[\text{Ph}_2\text{CH} \cdot][\cdot\text{S}_x \cdot] = 0 \quad (iii)$$

$$d[\text{HS}_x \cdot]/dt = k_2'[\text{MSH}][\cdot\text{S}_x \cdot] - k_3[\text{HS} \cdot] + k_5[\text{Ph}_2\text{CHS}_x \cdot] = 0 \quad (iv)$$

$$d[\text{HS} \cdot]/dt = k_3[\text{HS}_x \cdot] - k_4'[\text{MSH}][\text{HS} \cdot] = 0 \quad (v)$$

$$d[\text{Ph}_2\text{CHS}_x \cdot]/dt = k_5[\text{Ph}_2\text{CH} \cdot][\cdot\text{S}_x \cdot] - k_6[\text{Ph}_2\text{CHS}_x \cdot] - k_7[\text{Ph}_2\text{CHS}_x \cdot]^2 = 0 \quad (vi)$$

Using relations (iii) and (v),  $k_5[\text{Ph}_2\text{CH}\cdot][\cdot\text{S}_{x\cdot}]$  and  $k_3[\text{HS}_{x\cdot}]$  in (i), (iv) and (vi) are replaced by  $k_4''[\text{MS}\cdot][\text{Ph}_2\text{CH}_2]$  and  $k_4'[\text{MSH}][\text{HS}\cdot]$ , respectively. Then the relations (i), (iv) and (vi) lead to (i)', (iv)' and (vi)', respectively. From (i)', (iv)' and (vi)',

$$k_{11}[\text{MS}\cdot][\text{S}_8] = k_7[\text{Ph}_2\text{CHS}_{x\cdot}]^2 \quad (\text{vii})$$

From (i)' and (ii),

$$\begin{aligned} k_{11}[\text{MS}\cdot][\text{S}_8] - 2k_2'[\text{MSH}][\cdot\text{S}_{x\cdot}] - 2k_{10}[\text{MSSM}] \\ - 2k_{13}[\text{MSSM}][\cdot\text{S}_{x\cdot}] = 0 \end{aligned} \quad (\text{viii})$$

From (iv)' and (vi)',

$$\begin{aligned} k_4''[\text{MS}\cdot][\text{Ph}_2\text{CH}_2] + k_2'[\text{MSH}][\cdot\text{S}_{x\cdot}] - k_4'[\text{MSH}][\text{HS}\cdot] \\ - k_7[\text{Ph}_2\text{CHS}_{x\cdot}]^2 = 0 \end{aligned} \quad (\text{ix})$$

At a stationary state  $[\text{MS}\cdot]$  is constant, and  $[\text{S}_8]$  is also constant at the initial stage of the reaction, only because  $\text{S}_8$  consumption is much less as compared with its concentration. Therefore, at a stationary state, especially at the initial stage, the relation

$$k_{11}[\text{MS}\cdot][\text{S}_8] = c \quad (15)$$

holds, where  $c$  represents a constant. This relation is essential to solve the equation and will be discussed later in detail. From (15) and (viii),

$$[\cdot\text{S}_{x\cdot}] = \frac{c - 2k_{10}[\text{MSSM}]}{2\{k_2[\text{MSH}] + k_{13}[\text{MSSM}]\}} \quad (\text{x})$$

The rate equation for MBTS consumption is as follows.

$$-d[\text{MSSM}]/dt = k_{10}[\text{MSSM}] + k_{13}[\text{MSSM}][\cdot\text{S}_{x\cdot}] \quad (\text{xi})$$

The rate equation for the formation of MBT is also indicated below.

$$d[\text{MSH}]/dt = k_4''[\text{MS}\cdot][\text{Ph}_2\text{CH}_2] - k_2'[\text{MSH}][\cdot\text{S}_{x\cdot}] - k_4'[\text{MSH}][\text{HS}\cdot]$$

Putting (ix), (vii) and (viii) in the above equation in this order,

$$d[\text{MSH}]/dt = 2k_{10}[\text{MSSM}] + 2k_{13}[\text{MSSM}][\cdot\text{S}_{x\cdot}] \quad (\text{xii})$$

Comparing the relation (xi) with (xii),

$$-d[\text{MSSM}] = d[\text{MSH}]/2$$

Hence,

$$[\text{MSSM}]_0 - [\text{MSSM}] = [\text{MSH}]/2 \quad (16)$$

where  $[\text{MSSM}]_0$  represents initial concentration of MBTS.

Putting (x) in (xi),

$$-d[\text{MSSM}]/dt = \frac{[\text{MSH}] + (k_{13}/2k_{10}k_2')c}{[\text{MSH}] + (k_{13}/k_2)[\text{MSSM}]} \cdot k_{10}[\text{MSSM}] \quad (\text{xiii})$$

Putting (16) in (xiii),

$$-\frac{[\text{MSSM}]_0 - (1 - k_{13}/2k_2')[\text{MSSM}]}{[\text{MSSM}]_0 + c'/2 - [\text{MSSM}]} \cdot \frac{d[\text{MSSM}]}{[\text{MSSM}]} = k_{10}dt \quad (\text{xiv})$$

where

$$c' = ck_{13}/2k_{10}k_2' \quad (17)$$

Integrating (xiv),

$$\begin{aligned} & \frac{[\text{MSSM}]_0}{[\text{MSSM}]_0 + c'/2} \cdot \log \left\{ \frac{[\text{MSSM}]_0}{[\text{MSSM}]} \cdot \frac{[\text{MSSM}]_0 + c'/2 - [\text{MSSM}]}{c'/2} \right\} \\ & - (1 - k_{13}/2k_2') \log \frac{[\text{MSSM}]_0 + c'/2 - [\text{MSSM}]}{c'/2} = k_{10}t \end{aligned}$$

At the initial stage of the reaction  $[\text{MSSM}]$  is nearly equal to  $[\text{MSSM}]_0$ , then

$$\frac{[\text{MSSM}]_0 + c'/2 - [\text{MSSM}]}{c'/2} = 1$$

Hence, at this stage the following simple equation is obtained in place of the rather complex one cited above.

$$\log \frac{[\text{MSSM}]_0}{[\text{MSSM}]} = \frac{[\text{MSSM}]_0 + c'/2}{[\text{MSSM}]_0} \cdot k_{10}t \quad (18)$$

If one considers that the induced decomposition (13) does not occur,  $k_{13}$  in (17) becomes zero, and (18) leads to (19) cited below.

$$\log \frac{[\text{MSSM}]_0}{[\text{MSSM}]} = k_{10}t \quad (19)$$

Whether (18) or (19) can interpret the results will be indicated in the next section.

As stated above the accelerating efficiency of MBTS is represented by  $d([\text{H}_2\text{S}] + [\text{MSH}]/2)/dt$ . From the reaction sequence cited above,

$$d[\text{H}_2\text{S}]/dt = k'_4[\text{MSH}][\text{HS}\cdot] = k'_2[\text{MSH}][\cdot\text{S}_x\cdot] + k_6[\text{Ph}_2\text{CHS}_x\cdot] \quad (\text{xv})$$

From (vii) and (15),

$$[\text{Ph}_2\text{CHS}_x\cdot] = (c/k_7)^{\frac{1}{2}} \quad (\text{xvi})$$

From (xv), (xvi) and (x),

$$d[\text{H}_2\text{S}]/dt = \frac{k'_2[\text{MSH}](c - 2k_{10}[\text{MSSM}])}{2\{k'_2[\text{MSH}] + k_{13}[\text{MSSM}]\}} + k_6(c/k_7)^{\frac{1}{2}} \quad (20)$$

The accelerating efficiency  $d([\text{H}_2\text{S}] + [\text{MSH}]/2)/dt$  can be calculated from (20) and (xii).

$$d([\text{H}_2\text{S}] + [\text{MSH}]/2)/dt = c/2 + k_6(c/k_7)^{\frac{1}{2}} \quad (21)$$

Since MBTS disappears completely at the final stage of the reaction,  $[\text{MSSM}]$  in (20) is equal to zero at this stage. Then (20) leads to (22),

$$d[\text{H}_2\text{S}]/dt = c/2 + k_6(c/k_7)^{\frac{1}{2}} \quad (22)$$

Comparing (21) with (22), it is clearly understood that MBTS is completely converted to MBT after the long reaction time and that MBT formed corresponds to  $(1/2)\text{H}_2\text{S}$  with regard to hydrogen abstraction from DPM.

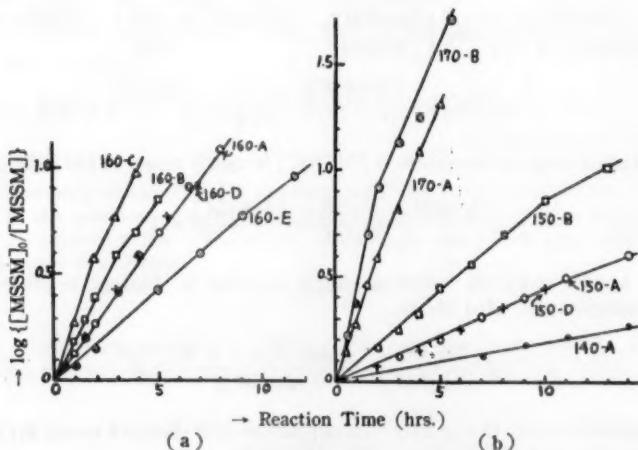


FIG. 1a and FIG. 1b.—Rates of MBTS consumption.

At relatively lower temperatures,  $k_{11}$  is assumed to be sufficiently smaller as compared with  $k_6$  or  $k_7$ . Considering the relation  $c = k_{11}[\text{MS} \cdot ][\text{S}_8]$ , the following relation may hold under this condition.

$$c/2 \ll k_6(c/k_7)^{\frac{1}{2}}$$

Then, (21) and (22) are simplified respectively as follows.

$$d([\text{H}_2\text{S}] + [\text{MSH}]/2)dt = k_6(c/k_7)^{\frac{1}{2}} \quad (23)$$

$$d[\text{H}_2\text{S}]/dt = k_6(c/k_7)^{\frac{1}{2}} \quad (24)$$

The value  $c$  of accelerating efficiency of MBTS will be determined experimentally in the next section.

*Comparison of theoretical equations with experimental results.*—Figure 1 shows  $\log ([\text{MSSM}]_0 / [\text{MSSM}])$  in (18) or (19) versus reaction time. The values of  $[\text{MSSM}]$  can be obtained from (16) by determining  $[\text{MSH}]$ . In succeeding experiments symbols 140-A, 150-B, 160-C, etc. are used. Figures indicate temperatures at which the reaction is conducted, and letters show initial concentrations of MBTS and  $\text{S}_8$  as summarized in Table II.

Figure 1 indicates that at the initial stage,  $\log ([\text{MSSM}]_0 / [\text{MSSM}])$  is in

TABLE II  
INITIAL CONCENTRATIONS OF MBTS AND S<sub>8</sub> IN MOLES/LITER

	A	B	C	D	E
[MSSM] <sub>0</sub> (mole/l)	0.142	0.072	0.036 <sub>4</sub>	0.1425	0.271
[S <sub>8</sub> ] <sub>0</sub> (mole/l)	0.142	0.144 <sub>4</sub>	0.145 <sub>4</sub>	0.0718	0.271

linear relation versus reaction time and that the slope of the straight line is dependent on [MSSM]<sub>0</sub>. The latter result can not be interpreted by (19). If one considers that the value of  $c'$  is constant under a given condition but varies with various [MSSM]<sub>0</sub>, the result can be interpreted by (18). Changes of  $c'$  with [MSSM]<sub>0</sub> are indicated in Table III below. The slopes of straight lines indicated in Figure 1 give the values of  $([MSSM]_0 + c'/2)k_{10}/[MSSM]_0$ .

TABLE III  
THE RELATION OF  $c$  VALUES WITH [MSSM]<sub>0</sub>

No.	[MSSM] <sub>0</sub> (mole/l)	$k_8(c/k_7)^{\frac{1}{2}}$ (mole/l)	$(k_8^2/k_7)c \cdot 10^4$
160-A	0.142	0.03	9.0
160-B	0.072	0.022	4.8
160-C	0.0362	0.018	3.2

The values of  $\log \{([MSSM]_0 + c'/2)k_{10}/[MSSM]_0\}$  of series A and B at various temperatures were plotted versus  $1/T$  in Figure 2. If one considers that the distance parallel to the ordinate between the two straight lines represents the difference in the values of  $\log \{([MSSM]_0 + c'/2)/[MSSM]_0\}$  between series A and B, the apparent activation energy of the thermal dissociation of MBTS can be obtained from Figure 2. This was found to be 32.7 kcal/mole.

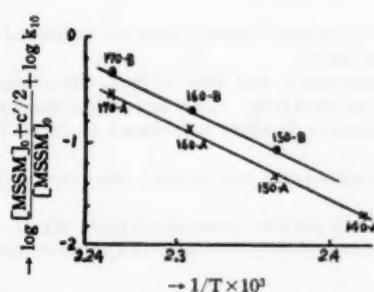


FIG. 2.— $\log \{([MSSM]_0 + c'/2)k_{10}/[MSSM]_0\}$  values of series A and B versus  $1/T$  curves.

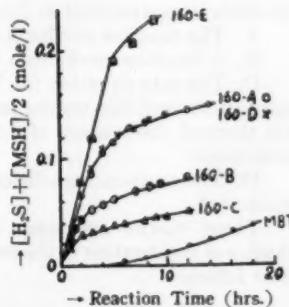


FIG. 3.—Accelerating efficiency ( $[H_2S] + [MSH]/2$ ) of MBTS.

The values of  $\{[H_2S] + [MSH]/2\}$  in mole/l were plotted versus reaction time in Figure 3. Figure 3 shows that (23) interprets the results satisfactorily. The slopes of the straight lines which appeared at the initial stage of the reaction give the values of  $k_8(c/k_7)^{\frac{1}{2}}$ . These values together with [MSSM]<sub>0</sub> are summarized in Table III.

Table III shows that the value of  $c$  increases to a lesser extent than that of [MSSM]<sub>0</sub>. When the authors interpreted the results of Figure 1 by (18),

they assumed that the change of  $c'$  was less than that of  $[\text{MSSM}]_0$ . This assumption was verified here experimentally, since  $c'$  is proportional to  $c$  as (15) indicates.

Figure 3 also indicates that at the final stage of the reaction the slopes of the lines approach those for MBT. For comparison, one of the results with MBT, which was already indicated in Figure 1a of Part IV, is shown again in Figure 3 of this paper. As already indicated in Part IV the accelerating efficiency of MBT, i.e.,  $d[\text{H}_2\text{S}]/dt$ , is independent of  $[\text{MSH}]$  at its very high concentration. The result that the slopes of the lines of MBTS approach to those for MBT at the final stage of the reaction has been already interpreted by (22) or (24). The hydrogen sulfide rate equation for the lower temperature reaction involving DPM, sulfur and MBT has been already indicated in Part IV and is again cited below.

$$d[\text{H}_2\text{S}]/dt = k_6 \{ (1 + m)/m \}^{1/2} \cdot (k_1/k_7)^{1/2} [\text{S}_8]^{1/2}$$

Comparing this equation with (24),

$$c = (1 + m)/m \cdot k_1 [\text{S}_8]$$

Therefore, it is concluded that the value of  $c$  varies as the reaction proceeds, and that there are two sorts of stationary state, namely initial and final, in this reaction. In previous paper  $m$  was defined as acceleration coefficient of mercaptan type accelerator. In this paper  $c$  should be defined as the acceleration coefficient of a bis-type accelerator.

### SUMMARY

The reaction involving diphenylmethane, sulfur and 2,2'-benzothiazolyl disulfide is summarized as follows.

- A. The reaction products and material balance among them are indicated.
- B. A reaction mechanism was decided upon.
- C. The rate equation for MBTS consumption was derived from the above mechanism and the results interpreted satisfactorily. The activation energy for thermal dissociation of 2,2'-benzothiazolyl disulfide was found to be 32.7 kcal/mole.
- D. The accelerating efficiency of this accelerator was defined, discussed and evaluated.

These studies are being continued and further communications on the studies of accelerators in the presence of zinc oxide or zinc soap will appear in the near future.

### SYNOPSIS

The reaction involving diphenylmethane, sulfur and 2,2'-benzothiazolyl disulfide (accelerator) in the absence of zinc oxide was investigated. The reaction products derived from diphenylmethane did not differ from those in the absence of accelerator nor from those in the presence of 2-mercaptopbenzothiazole. However, 2,2'-benzothiazolyl disulfide increased the amounts of the products remarkably as compared with 2-mercaptopbenzothiazole. The former was converted to the latter during the reaction. The accelerating mechanism involved mercaptobenzothiazolyl radicals which were generated by homolytic dissociation of 2,2'-benzothiazolyl disulfide and which split the  $\text{S}_8$  ring molecule.

The rate of accelerator consumption was calculated and compared with the experimental results. The accelerating efficiency was defined and determined.

#### ACKNOWLEDGMENT

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# REACTION BETWEEN DIPHENYLMETHANE AND 2,2'-DIBENZOTHIAZOLYL DISULFIDE \*

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## INTRODUCTION

In a fundamental study of vulcanization and acceleration the authors have attempted to use diphenylmethane as a model of rubber hydrocarbon. The reaction between diphenylmethane (DPM) and sulfur has been reported in earlier papers<sup>1</sup>. As a preliminary step to the study of the mechanism of acceleration, the interaction of 2,2'-dibenzothiazolyl disulfide (MBTS) with DPM is reported in this paper. It is well known that the benzothiazolyl group is very stable at vulcanization temperatures, and that MBTS and 2-mercaptobenzothiazole (MBT) are converted to zinc mercaptide after vulcanization in the presence of zinc oxide<sup>2</sup>, while guanidine type and thiuram type accelerators are known to decompose more or less at vulcanization temperature. This is the reason why the authors started their investigation with a thiazole type accelerator.

Recently Moore<sup>3</sup> reported the reaction between MBTS and olefins such as cyclohexene. However, it is important to obtain knowledge on the interaction of diphenylmethane with this accelerator.

## RESULTS AND DISCUSSION

*Products at 160° C.*—A mixture of DPM and MBTS was heated at 160° C in a stream of nitrogen gas. During the reaction no evolution of hydrogen sulfide was recognized. The reaction products are given in Table I. After the reaction times indicated, the starting material, MBTS, was not found among the products.

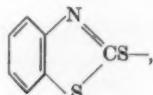
From the results of Table I the balance sheet of benzothiazolyl groups in the starting material and final products may be obtained. Benzothiazolyl groups in the final products are distributed among MBT, MSCHPh<sub>2</sub>, MNCHPh<sub>2</sub>, MSM and MNM molecules. However, both MSM and MNM and the starting material MBTS have two of these groups and the others have only one. This group in the products after 20 hours amounts to 34.8 m moles in all, and that after 40 hours to 32.3 m moles. Therefore, more than 80% of the MBTS can be said to have been recovered in the final products. The mechanism of formation of the products will be discussed in the succeeding sections.

*Mechanism of the reaction at 140° C.*—Moore<sup>3</sup> has already reported the mechanism of the interaction of cyclohexene with MBTS. According to the mechanism proposed by him the primary reaction products between DPM and MBTS are MBT, MSCHPh<sub>2</sub>, MNCHPh<sub>2</sub> and tetraphenylethane, all of which are indicated in Table I. The mechanism of the reaction is shown by Equations (1) to (4).

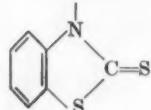
\* Translated by J. Tsurugi from *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)* **60**, 362 (1957).

TABLE I  
REACTION PRODUCTS OF DPM (200 M MOLE) AND MBTS (20 M MOLE) AT 160° C

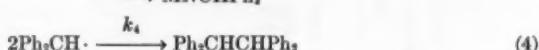
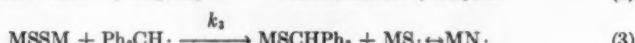
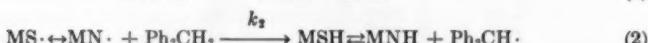
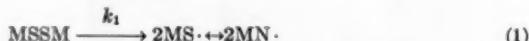
Ultraviolet absorption spectra<sup>4</sup> show that MBTS has a structure of type MSSM; on the other hand, MBT has proved to be a tautomer of type  $\text{MSH} \rightleftharpoons \text{MN}\text{M}$ <sup>4,5,6</sup>. Symbol MS- represents the group



and MN- represents



Since each disulfide molecule is known in general to decompose thermally to two mercaptyl radicals, in the case of MBTS the radical must be stabilized by resonance of type  $(\text{MS}\cdot \leftrightarrow \text{MN}\cdot)$ .



From the reaction sequence the dissipating rate equation of MBTS,

$$-\frac{d[\text{MSSM}]}{dt} = k_1[\text{MSSM}] + k_3(2k_1/k_4)^{\frac{1}{2}}[\text{MSSM}]^{\frac{1}{2}} \quad (5)$$

was derived by the stationary state method. If one considers that the chain length is very long, then the first term of this equation can be neglected as compared with the second term. Then,

$$-\frac{d[\text{MSSM}]}{dt} = k_3(2k_1/k_4)^{\frac{1}{2}}[\text{MSSM}]^{\frac{1}{2}}$$

is obtained, which on integration gives

$$[\text{MSSM}]_t^{-\frac{1}{2}} - [\text{MSSM}]_0^{-\frac{1}{2}} = 0.5k_3(2k_1/k_4)^{\frac{1}{2}} \cdot t, \quad (6)$$

where  $[\text{MSSM}]_t$  and  $[\text{MSSM}]_0$  represent the concentration of MBTS after  $t$  hours and initial concentration, respectively. For long chains one mole of MBT is produced from one mole of MBTS as indicated by Equations (2) and (3). Then the relation

$$[\text{MSSM}]_0 - [\text{MSSM}]_t = [\text{MSH}]_t$$

is obtained, where  $[\text{MSH}]_t$  represents the concentration of MBT after  $t$  hours. From the above equation,  $[\text{MSSM}]_t$  can be calculated by determining  $[\text{MSH}]_t$ .

TABLE II

MBT PRODUCED VERSUS REACTION TIME FOR DPM (500 M MOLE)  
AND MBTS (50 M MOLE) AT 140° C

Time, hr [MSH] · 10 <sup>3</sup> (mole/l)	7	10	13	16	19	22
	7.6	13.5	21	27.5	30.7	34.5

At a lower temperature where no decomposition of the primary products would be recognized, the yield of  $[MSH]_t$  should be determined as a function of time. At 140° C the reaction mass had pale green color after a long time. Since TBP is known to have a deep blue color<sup>1</sup>, and since it will be experimentally proved later that the decomposition of the primary product is accompanied

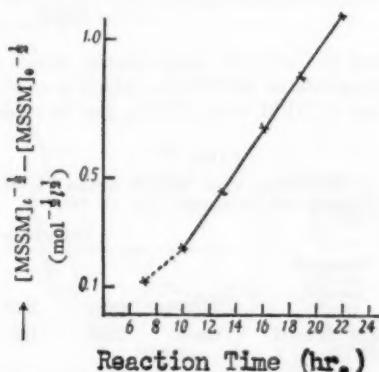


FIG. 1.—Values of  $\{[(MSSM)_{t-}^{1/2} - (MSSM)_{0-}^{1/2}]\}$  versus time curve at 140° C.

by the formation of TBP, it can be said that no appreciable decomposition occurred at this temperature. Table II indicates the amounts of MBTS determined during the reaction at 140° C in the stream of nitrogen gas. A straight line in Figure 1, which was obtained from the data of Table II, indicates that the kinetic Equation (6) holds over an extensive range of the reaction. The composite rate constant  $k_3 (2k_1/k_4)^{1/2}$  has a value of  $3.88 \times 10^{-5}$  mole<sup>-1/2</sup> sec<sup>-1</sup> at 140° C, while in the reaction of MBTS with cyclohexene at 139° C<sup>3</sup> it has a value of  $9.5 \times 10^{-5}$ .

*Decomposition of the primary products at 160° C.*—Table III indicates that

TABLE III

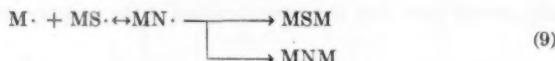
ISOMERIZATION OF MSCHPh<sub>2</sub> OR MNCHP<sub>2</sub> IN A STREAM OF NITROGEN GAS AT 160° C

Starting material, g	Time, hr	Products, g	
		MSCHPh <sub>2</sub>	MNCHP <sub>2</sub>
MSCHPh <sub>2</sub> , 1	5	0.8	0.13
	15	—	0.8
MNCHP <sub>2</sub> , 1 DPM*, 10	15	0.51	0.21

\* DPM was used as a solvent, since MNCHP<sub>2</sub> had too high a melting point, 181–182° C; see experimental.

simple heating of  $\text{MSCHPh}_2$  or  $\text{MNCHPh}_2$  leads only to isomerization. However, Table IV shows that heating of  $\text{MSCHPh}_2$  in the presence of MBTS resulted in the decomposition of  $\text{MSCHPh}_2$ .

The results of Table IV for the decomposition of  $\text{MSCHPh}_2$  in the presence of MBTS is interpreted by a radical mechanism as follows.



The products indicated in Table IV were already shown in Table I as well. Therefore, the decomposition of  $\text{MSCHPh}_2$ , which is one of the primary products of the interaction of DPM with MBTS, can be explained by the mech-

TABLE IV  
INTERACTION OF  $\text{MSCHPh}_2$  WITH MBTS AFTER 15 HOURS IN THE  
STREAM OF NITROGEN GAS AT  $160^\circ \text{C}$

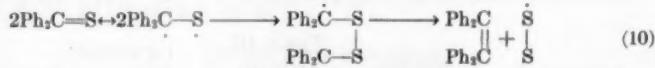
Starting material, m mole	Unreacted starting material, m mole	Products, m mole				
		$\text{MNCHPh}_2$	MBT	TBP	MSM	Tetraphenyl- ethane
$\text{MSCHPh}_2, 9 \}$	$\text{MSCHPh}_2, 5$	trace	2.04	0.8	1	0.1
MBTS, 4.5	MBTS, 1					

anism indicated by Equations (7) to (9). However, in the reaction system of DPM and MBTS the radical  $\text{Ph}_2\text{CH}\cdot$  which is produced by Equations (2), cited before, also may dehydrogenate  $\text{MSCHPh}_2$  as follows.



Thus the mechanism of formation of the products is explained by Equations (1) to (4) and Equations (7), (7'), (8) and (9) except for tetraphenylethylene.

It has been already reported by one of the authors<sup>1</sup> that tetraphenylethylene is produced by pyrolysis of TBP.



The radical  $\cdot\text{S}-\text{S}\cdot$  thus produced must lead to free sulfur molecules or result in dibenzhydryl polysulfides which were reported to be the main product between DPM and sulfur radicals. Neither free sulfur nor polysulfide could be found in the products, as already stated, probably because of the small quantity.

## EXPERIMENTAL

*Materials and synthesis of authentic samples.*—Commercial 2,2'-dibenzo-thiazolyl disulfide (MBTS) was recrystallized several times to constant melting

point of 179° C. Synthesis and properties of four authentic specimens are as follows.

*2-(Benzhydrylthio)benzothiazole* (MSCHPh<sub>2</sub>) was prepared from the mercaptide of MBT and diphenylbromomethane in toluene by the method of Moore<sup>8</sup>. White leaflets, m. p. 110–111° C, yield 70%. C<sub>20</sub>H<sub>16</sub>S<sub>2</sub>: N % calcd. 4.20, found 4.19. The ultraviolet absorption spectra (Figure 2) showed that this is a 2-substituted benzothiazole.

*2-Thio-3-(benzhydryl) benzothiazoline* (MNCHPh<sub>2</sub>). Heating of MSCHPh<sub>2</sub>, as indicated in Table III, gave a mixture of leafletlike and needlelike crystals. The former was more soluble in benzene and the remainder was recrystallized from alcohol, m. p. 181–182° C. C<sub>20</sub>H<sub>16</sub>S<sub>2</sub>: N % calcd. 4.20, found 4.16. This was found to be a 3-substituted 2-thiobenzothiazoline from ultraviolet (U V) absorption spectra (Figure 2).

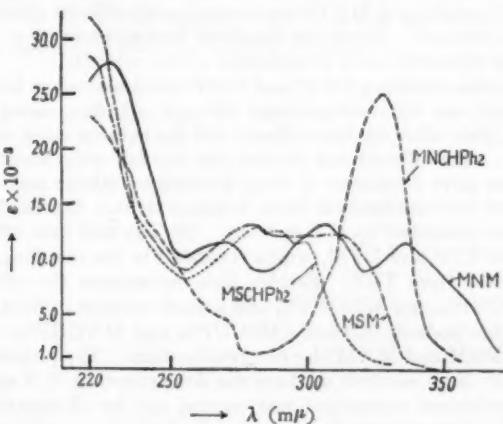


FIG. 2.—Ultraviolet absorption spectra of four authentic specimens.

*2,2'-Dibenzothiazolyl monosulfide* (MSM) was prepared from two moles of 2-chlorobenzothiazole and one mole of thiourea according to the literature<sup>7</sup>, recrystallized from methanol to give white silklike crystals, m. p. 101.5° C (lit.<sup>7</sup> 101.5° C).

*2-Thio-3-(2'-benzothiazolyl) benzothiazoline* (MNM). Isomerization of MSM was carried out at 200° C for 15 hours under nitrogen gas. Isolation of one isomer from the other by recrystallization was difficult because of their similar appearance. The isomeric mixture in benzene was chromatographed through an alumina column and the effluent was divided into several fractions. Some fractions which on evaporation of benzene gave solid having the highest melting point were gathered together and again chromatographed in benzene solution. Thus pale yellow silklike crystals were obtained, m. p. 138° C. Since U V spectra before and after recrystallization coincided completely this substance was considered to be pure. C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>S<sub>2</sub>: N % calcd. 9.32, found 9.35. Ultraviolet absorption spectra (Figure 2) showed that this compound is a 3-substituted 2-thiobenzothiazoline, while the starting material MSM is 2,2'-dibenzothiazolyl monosulfide.

*Isolation and estimation of the products.—Reaction of DPM and MBTS.* DPM and MBTS were heated in a ground jointed flask under nitrogen gas. The needlelike crystals which appeared in the reaction mass after cooling to room temperature were filtered. By distilling the filtrate under reduced pressure, DPM and TBP were obtained, the latter was identified and estimated as 2,4-dinitrophenylhydrazone. The residue of distillation will be mentioned later. The needlelike crystals were found to be MBT. Estimation of MBT was as follows. The crystals were dissolved in benzene and the benzene solution was shaken with aqueous basic lead acetate solution. The precipitate was filtered, washed and suspended again in benzene, and then shaken with acetic acid. The benzene solution was washed, dried and after evaporation of benzene gave pale yellow crystals, m. p. 178° C., mixed m. p. with an authentic sample (commercial MBT recrystallized several times from methanol) 178° C. This procedure can be said to be almost quantitative. For example, a mixture of 0.1 g of MBT and 0.1 g of MBTS was treated as mentioned above, then 0.098 g of MBT was obtained. From the filtrate of lead mercaptide of MBT, 0.095 g of MBTS was recovered after evaporation of the solvent.

The residue after distilling DPM and MBT was dissolved in benzene. The benzene solution was chromatographed through alumina, using benzene as solvent at first, then after the blue effluent left the column using alcohol as the elution solvent. The effluent was divided into the following fractions. (1) The colorless effluent gave a mixture of sym. tetraphenylethane and tetraphenylethylene. After recrystallization from benzene-alcohol the mixture of both components was estimated by U V spectra. (2) The pale blue effluent gave a small amount of TBP and DPM, which remained in the distilling flask. The blue color resulted from TBP. Besides these substances the effluent gave a mixture of MSCHPh<sub>2</sub> and MNCHPh<sub>2</sub> and a small amount of mixture of MSM and MNM. One isomeric mixture (MSCHPh<sub>2</sub> and MNCHPh<sub>2</sub>) was isolated from another (MSM and MNM) by recrystallization. The proportion of each respective isomer in an isomeric mixture was determined by U V spectra. Isolation of an individual compound was carried out by chromatography and identification by determining the m. p. and mixed m. p. with an authentic sample. (3) The pale green effluent gave silklike crystals besides a small amount of MSCHPh<sub>2</sub> which was isolated by recrystallization. The silklike crystals were found to be a mixture of MSM and MNM from analytical data, for which isolation, estimation and identification has already been indicated. (4) The brown effluent on evaporation of the solvent gave a mixture of MSM and MNM besides a brown oily substance, which on digestion with aqueous Na<sub>2</sub>SO<sub>3</sub> solution did not give dibenzhydryl disulfide<sup>1</sup>. Therefore, the oily substance is not dibenzhydryl polysulfides but is unidentified.

*Isomerization of MSCHPh<sub>2</sub>, or MNCHPh<sub>2</sub> and decomposition of MSCHPh<sub>2</sub>.* —For the decomposition the products were chromatographed directly following the separation of MBT. TBP was identified and estimated as 2,4-dinitrophenylhydrazone from the effluent. For the case of isomerization the procedure was similar.

*Kinetics.*—In a ground jointed flask equipped with a condenser, a nitrogen gas inlet tube and a thermometer, DPM and MBTS were heated in a stream of nitrogen gas. At a given time an aliquot was pipetted, weighed and analyzed for MBT content. On pipetting care should be taken to keep air from entering the flask.

## SUMMARY

At a lower temperature where no decomposition of the primary product occurred, the reaction mechanism is a radical chain reaction indicated by Equations (1) to (4).

At 160° C one of the primary products,  $\text{MSCHPh}_2$ , was decomposed to various secondary products by the radicals which were present in the reaction system. The decomposition mechanism is indicated by Equations (7) and (7') and from (8) to (11).

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# THE STRUCTURE AND ULTRAVIOLET ABSORPTION SPECTRA OF POLYSULFIDES \*

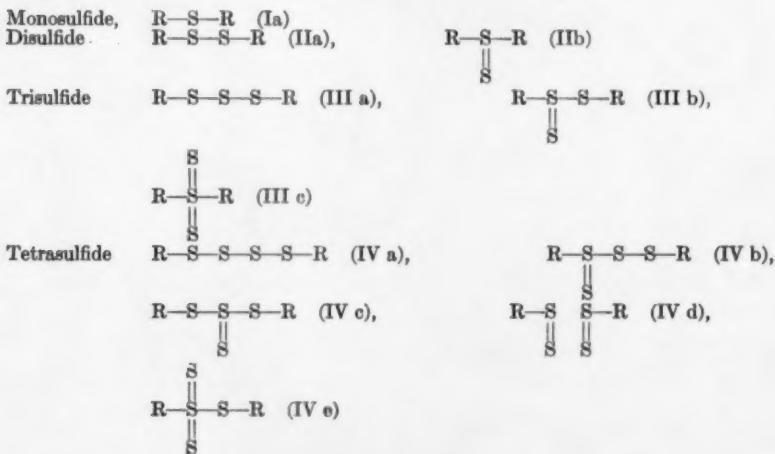
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## INTRODUCTION

The study of the chemical structure of organic polysulfidic compounds may help solve problems about sulfur-bridge vulcanizates, synthetic polysulfide rubbers and accelerators (i.e., thiuram and thiazole types).

Structures of organic polysulfides may be indicated in many ways, for example;



J. C. Patrick<sup>1</sup> and P. Frederic<sup>2</sup> considered from the standpoint of chemical behaviors that the sulfur atoms are linked together not in a line but in a branched form, as in IIb, IIIb, IVb, IVc, IVd, etc. However, from the studies on the electron diffraction of dimethyltrisulfide<sup>3</sup>, the ultraviolet absorption spectra of sulfides<sup>4,5</sup> and x-ray diffraction<sup>6</sup>, it is concluded that the arrangement of sulfur atoms is linear, as shown as Ia, IIa, IIIa, and IVa.

The present author has observed the ultraviolet spectra of the polysulfides, the results being reported for two series as follows:

(1) Dibenzyl mono-, di-, tri- and tetrasulfides; here it was found that a regular relationship between the number of sulfur atoms and the absorption exists, and it is assumed that the sulfur atoms are arranged as a chain.

\* Reprinted from the *Journal of the Institute of Polytechnics, Osaka City University, Vol. 5, Series C, pages 206-212 (1956). See also Reference 22.*

(2) *p,p'*-Ditoly mono-, di-, tri- and tetrasulfides; here it was found that the absorption exists at a longer wave length region than in the dibenzyl series, owing to the conjugation of the benzene ring with sulfur atoms. The regular relationship between the number of sulfur atoms and the absorption spectra was also observed, as in the case of dibenzyl polysulfides.

### EXPERIMENTAL

*Dibenzyl monosulfide*<sup>7</sup>.—Benzyl chloride (b.p. 179–180°) dissolved in alcohol was heated to about 60° and aqueous Na<sub>2</sub>S dropped in slowly and the reaction allowed to continue for 6 hours at 70°. After the reaction was completed, the oily product was separated and cooled. It solidified. Recrystallization from alcohol gave white crystals melting at 48.5°. *Analysis.* Found: C, 78.55, H, 5.92. Calcd.: C, 78.50, H, 6.54.

*Dibenzyl disulfide*<sup>8</sup>.—Sodium disulfide was prepared by adding the theoretical amount of sulfur to sodium sulfide and heating in a steam bath. It was dropped into an alcholic solution of benzyl chloride. The solution was kept for 10 hours at 70°. By cooling, the crystalline product was obtained from the lower layer. Recrystallization of the product from alcohol gave white crystals, m.p. 71°. *Analysis.* Found: C, 68.66, H, 5.17. Calcd.: C, 68.29, H, 5.69.

*Dibenzyl trisulfide*<sup>9</sup>.—Benzyl mercaptan was dissolved in anhydrous ether. Sulfur dichloride freshly distilled (b.p. 66–67°) was dropped into the ether solution. The reaction was carried out under stirring and cooling with ice, avoiding any rise of reaction temperature. By and by, crystals came out. Recrystallization from alcohol gave light-yellow needles, m.p. 49°. *Analysis.* Found: C, 60.48, H, 6.14. Calcd.: C, 60.43, H, 5.04.

*Dibenzyl tetrasulfide*<sup>10</sup>.—Sulfur monochloride (b.p. 136–137°) was used instead of sulfur dichloride in the previous reaction. Recrystallization from alcohol gave light yellow needle crystals, m.p. 54°. *Analysis.* Found: C, 54.6, H, 5.07. Calcd.: C, 54.02, H, 4.52.

*Dibenzyl*.—Benzyl chloride was treated with metallic sodium in anhydrous benzene. The recrystallization of the product from alcohol gave white crystals, m.p. 52°. *Analysis.* Found: C, 92.2, H, 7.5. Calcd.: C, 92.3, H, 7.7.

*p,p'-Ditoly monosulfide*<sup>11</sup>.—*p*-Toluidine was dissolved in hydrochloric acid, and aqueous sodium nitrite was added under cooling with ice. The diazonium chloride formed was made to react with aqueous sodium sulfide below 50°. The oily product was collected and distilled in a vacuum (175° C/16 mm Hg). Repeated recrystallization from alcohol gave white needle crystals, m.p. 57°. *Analysis.* Found: C, 78.71, H, 6.67. Calcd.: C, 78.50, H, 6.54.

*p,p'-Ditoly disulfide*<sup>12</sup>.—*p*-Thiocresol<sup>15</sup> (m.p. 43°) was dissolved in hydrochloric acid, ferric chloride was added and the mixture heated on a steam bath. Product was filtered and washed with dilute hydrochloric acid and water. Recrystallization from alcohol gave white needle crystals, m.p. 46°. *Analysis.* Found: C, 68.41, H, 5.72. Calcd.: C, 68.29, H, 5.69.

*p,p'-Ditoly trisulfide*<sup>13</sup>.—*p*-Thiocresol<sup>15</sup> was dissolved in anhydrous ether, and sulfur dichloride dissolved in ether was added under cooling and stirring. The product was collected and recrystallized from ether or alcohol. Light yellow plate crystals, m.p. 76°, were obtained. *Analysis.* Found: C, 60.20, H, 5.31. Calcd.: C, 60.43, H, 5.40.

*p,p'-Ditoly tetrasulfide*<sup>14</sup>.—*p*-Thiocresol<sup>15</sup> was dissolved in anhydrous ether, and an ether soln. of sulfur monochloride (b.p. 136–137°) was added under

cooling and stirring. The product was purified from ether or alcohol, and yellow needle crystals were obtained, m.p. 75°. *Analysis.* Found: C, 54.59, H, 4.66. Calcd.: C, 54.2, H, 4.52.

*n*-Heptane<sup>16</sup> was agitated with fuming sulfuric acid for several days, washed with alkaline solution and water, then dried with sodium sulfate, and distilled. B.p. of *n*-heptane thus obtained was 97–98.5°.

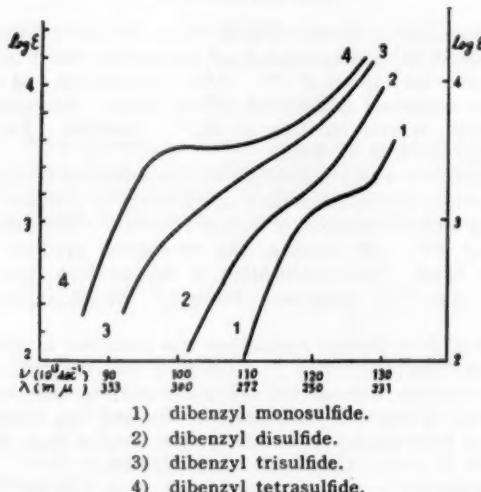


FIG. 1.—Ultraviolet absorption spectra of dibenzyl mono-, di-, tri- and tetrasulfides.

The ultraviolet absorption spectra in *n*-heptane solution were observed with a Shimazu QF-60 quartz spectrograph photometer with Fuji Process plate. The light source used was an iron spark.

#### RESULTS AND DISCUSSIONS

Figure 1 shows the absorption spectra of dibenzyl mono-, di-, tri- and tetrasulfides. As can be seen from these curves, each absorption spectrum of di-

TABLE I

$R = \text{C}_6\text{H}_4-\text{CH}_2-$	$R-\text{S}-R$	$R-\text{S}_2-\text{R}$	$R-\text{S}_3-\text{R}$	$R-\text{S}_4-\text{R}$
Wave length $\lambda$ ( $\mu$ )	244	258	272	286
Vibration number $\nu$ ( $10^{13} \text{ sec}^{-1}$ )	123	116.5	110	105
Intensity ( $\log \epsilon$ )	3.17	3.19	3.33	3.5

benzyl sulfides has a shoulder, but no peak. Intensities and wave lengths of these shoulders are given in Table I.

Figure 2 shows the absorption spectra of *p,p'*-ditolyl mono-, di-, tri- and tetrasulfides and *p*-thiocresol. The absorption spectra of ditolyl sulfides have the special shoulders and peaks at about 240  $\mu$ . Intensities and wave lengths of these shoulders and peaks are given in Table II.

Below 220  $\mu$ , other peaks may exist, but were not observed. The spec-

trum of dibenzyl was taken in order to find the role of the benzyl group in the absorption spectra of the dibenzyl series. The result is seen in Figure 3;  $\lambda_{\max}$  is 263 m $\mu$  and  $\log \epsilon$  is 2.79. Figure 3 contains also the data of Castilles<sup>17</sup> for comparison.

In the benzyl polysulfides, comparing Figure 1 with Figure 3, it may be concluded that the shoulders do not depend on the benzyl group, but on the

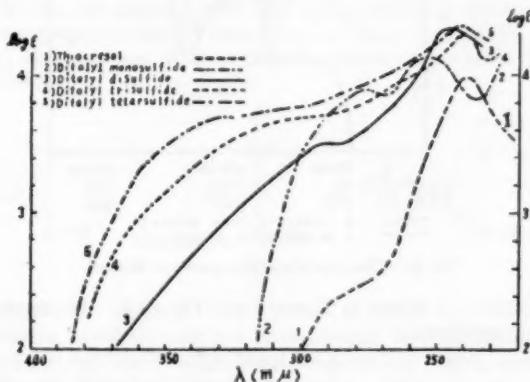


FIG. 2.—Ultraviolet absorption spectra of ditolyl mono-, di-, tri- and tetrasulfides and *p*-thioeresol.

sulfur atoms in the polysulfides, that is, on the lability of the lone electron pair of the sulfur atoms. The benzene nucleus can not conjugate with the sulfur atom, owing to the presence of the —CH<sub>2</sub>— between them.

As observed from Figure 1 and Table I, the site of the shoulder in the absorption spectrum of dibenzyl polysulfide moves with the number of combined sulfur atoms to longer wave lengths and the intensity of the shoulder increases.

In ditolyl polysulfides, the peaks observed between 240 m $\mu$  and 260 m $\mu$  are influenced by the number of sulfur atoms. As the number of sulfur atoms in-

TABLE II

$R = C_6H_5-\text{C}_6H_4-$	$R-SH$	$R-S-R$	$R-S_2-R$	$R-S_3-R$	$R-S_4-R$
Shoulder wave length $\lambda$ (m $\mu$ )	275	277	295	313	331
Intensity ( $\log \epsilon$ )	2.45	3.90	3.5	3.64	3.68
Peak wave length $\lambda$ (m $\mu$ )	239	254	243	241	240
Intensity ( $\log \epsilon$ )	3.90	4.14	4.34	4.30	4.36

creases, the position of the peak moves to a shorter wave length and the intensity at the peak increases. It may be concluded, however, that the peaks are due to the tolyl groups; thus  $\lambda_{\max} = 251.5$  m $\mu$ <sup>18</sup> for diphenyl compares with  $\lambda_{\max} = 250$  m $\mu$ <sup>19</sup> for diphenylsulfide.

As shown in Figure 2 and Table II, the sites of the shoulders observed between 270 m $\mu$  and 330 m $\mu$  in ditolylpolysulfide, move regularly to longer wave length with the increase in number of sulfur atoms. This shift of the sites of the shoulders depends on the lability of the lone electron pair of the sulfur atoms.

There is a regular relationship between the number of sulfur atoms and the

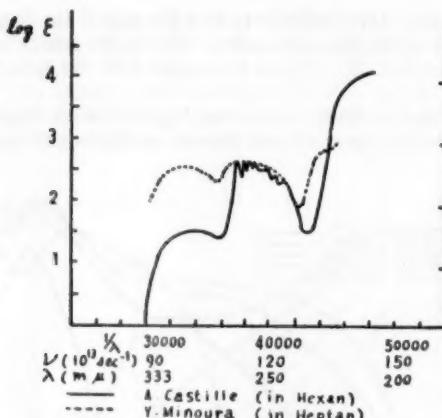


FIG. 3.—Ultraviolet absorption spectra of dibenzyl.

site of the shoulder, as shown in Figure 4 and Figure 5. An empirical formula can be written as follows:

$$\lambda_s = k_s n + \lambda_s^\circ$$

where  $n$  is the number of combined sulfur atoms,  $\lambda_s$  is the wave length of the shoulder of polysulfide, and  $k_s$  and  $\lambda_s^\circ$  are constants. The shift of the shoulder to longer wave length is 14 m $\mu$  by one sulfur atom in the dibenzyl series, and

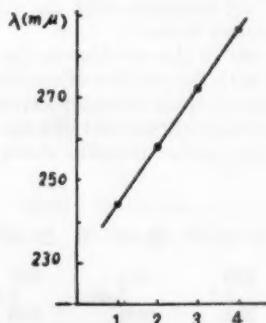
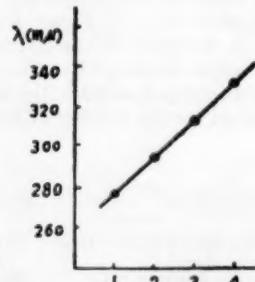


FIG. 4.—The relation between the number of sulfur atoms and the wave length of ultraviolet absorption spectra in dibenzyl polysulfides.

FIG. 5.—The relation between the number of sulfur atoms and the wave length of ultraviolet absorption spectra in *p,p'*-ditolyl polysulfides.

about 18 m $\mu$  in the ditolyl series. Therefore, in the benzyl sulfides series,  $k_s$  is 14 m $\mu$  and  $\lambda_s^\circ$  is 230 m $\mu$ . In ditolyl sulfides,  $k_s$  is 18 m $\mu$  and  $\lambda_s^\circ$  is 295 m $\mu$ .

These matters are similar to those in the series of the compounds R—(CH=CH) $_n$ —R, in which the following relations<sup>20,21</sup>, exist,

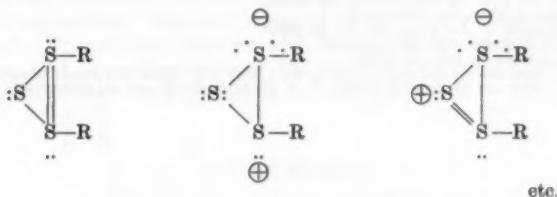
$$\lambda_p = k_p \sqrt{n} + \lambda_p^\circ \quad (\text{in polyene series})$$

$$\lambda_c = k_c n + \lambda_c^\circ \quad (\text{in cyanine series})$$

Intensities ( $\log \epsilon$ ) increases with the number of the group of  $(-\text{CH}=\text{CH}-)_n$ , as in the case of polysulfides. From these results, it may be reasonably assumed that  $-\text{S}-$  resembles  $-\text{C}=\text{C}-$ , and a sulfur atom in a polysulfide is a chain link as in the case of a polyene.

If the arrangement of sulfur atoms in the polysulfides is not in linear but in lateral linking, as in the formulas IIb, IIIb, IIIc, IVb, IVc and IVd, a regular relationship between  $\lambda_s$  and the number of sulfur atoms would not exist. Consequently it may be assumed that the sulfur atoms of dibenzyl and ditolyl polysulfides arrange themselves linearly as Ia, IIa, IIIa, and IVa.

Further, the presence of the following resonance hybrids might be considered to exist.



These structures, however, must not be important, because the regularity found in the absorption spectra of polysulfides, as described above, would be broken, if they made any important contribution.

### CONCLUSIONS

1. The ultraviolet absorption spectra of dibenzyl and ditolyl mono-, di-, tri-, and tetrasulfides were measured and the existence of a characteristic shoulder was clearly demonstrated.
2. It was found that the absorption peaks at 240–250 m $\mu$  are due to the tolyl groups in the tolyl sulfides.
3. A regular relationship was found between the number of combined sulfur atoms of dibenzyl and ditolyl polysulfides and the site of the shoulder of the absorption spectrum existed. It is expressed by the empirical formula

$$\lambda_s = k_s n + \lambda_s^0$$

The intensities ( $\log \epsilon$ ) of the absorption increase with the number of sulfur atoms.

4. There is a resemblance between the polyene series and the polysulfide series. Accordingly it is assumed that sulfur atoms link themselves into a chain.
5. The shoulders of the ditolyl polysulfides exist at longer wave lengths than these of the dibenzyl polysulfides. Their intensities are stronger in ditolyl series than in dibenzyl series. These facts may be arised from the conjugation of tolyl nucleus with sulfur atoms.

### ACKNOWLEDGMENT

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# THE STRUCTURE AND MOLECULAR REFRACTION OF ORGANIC POLYSULFIDES \*

YUJI MINOURA

In a previous paper<sup>1,2</sup>, the chain sulfur structures of polysulfides were inferred from the ultraviolet spectra of mono-, di-, tri- and tetra-sulfides in the benzyl and tolyl series. Ranband reported on the atomic refractions of sulfur compounds<sup>3</sup>. The author discusses here the molecular refraction of organic polysulfides, and from the results it has become clear that there is no side chain such as  $\text{---S---S---}$  in polysulfides.



## EXPERIMENTAL

**Materials.**—The materials were those reported in the previous papers<sup>1,2</sup>, benzyl monosulfide (m.p. 48.5°), benzyl disulfide (m.p. 71°), benzyl trisulfide (m.p. 49°), benzyl tetrasulfide (m.p. 54°), *p,p'*-ditolyl monosulfide (m.p. 57°), *p,p'*-ditolyl disulfide (m.p. 46°), *p,p'*-ditolyl trisulfide (m.p. 76°), *p,p'*-ditolyl tetrasulfide (m.p. 75°).

Carbon tetrachloride was dried over phosphorus pentachloride and distilled<sup>4</sup>.

**Measurements.**—After measuring the refractive index and density of solution and solvent, molecular refraction was calculated from the Lorenz-Lorenz equation. In the case of carbon tetrachloride, from the facts that the density is  $d_4^{20} = 1.59396$ , refractive index  $n_D^{20} = 1.4604$ , and molecular weight  $M_w = 153.48$ , the molecular refraction is  $R_D = 26.454$ . Refractive index was measured with sodium D-line as a light source and on Abbe refractometer (Goets make) at 20° C. Density was measured with Ostwald's aerometer.

## RESULTS AND DISCUSSION

The molecular refractions are given in Tables I to VIII where  $f$  is molar ratio,  $d$  is density,  $n_D$  is refractive index,  $R_D$  is molecular refraction.

As the refractive indexes of the benzyl and tolyl radicals are equal and for two of these radicals  $\div 60.5$ , the refractive index of  $S_n$  is calculated by subtracting 60.5 from the refractive index of any polysulfide.

TABLE I  
DIBENZYL MONOSULFIDE,  $M_w = 214.31$

$f$	$d_4^{20}$	$n_D^{20}$	$R_D$
0.00419	1.58997	1.4619	70.6
0.01122	1.58300	1.4643	70.6
0.01357	1.58145	1.4654	70.8
0.01581	1.57831	1.4660	71.6
			(70.5)

\* Reprinted from the *Journal of the Chemical Society of Japan, Pure Chemistry Section* 75, 869-871 (1954).

TABLE II  
DIBENZYL DISULFIDE  $M_w = 246.37$

<i>f</i>	$d_4^{20}$	$n_D^{\text{B}}$	$R_D$
0.00780	1.58653	1.4640	81.3
0.00868	1.58584	1.4645	81.5
0.00968	1.58498	1.4650	81.6
0.01183	1.58304	1.4660	81.6 (81.3)

TABLE III  
DIBENZYL TRISULFIDE  $M_w = 278.43$

<i>f</i>	$d_4^{20}$	$n_D^{\text{B}}$	$R_D$
0.00564	1.58862	1.4635	91.0
0.00714	1.58711	1.4643	91.3
0.00982	1.58509	1.4660	91.6
0.01244	1.58215	1.4671	90.9 (91.1)

TABLE IV  
DIBENZYL TETRASULFIDE  $M_w = 310.49$

<i>f</i>	$d_4^{20}$	$n_D^{\text{B}}$	$R_D$
0.00683	1.58821	1.4649	100.2
0.00994	1.58555	1.4671	101.5
0.01290	1.58250	1.4693	101.5
0.01481	1.58202	1.4707	102.0 (100.2)

TABLE V  
*p,p'*-TOLYL MONOSULFIDE  $M_w = 214.31$

<i>f</i>	$d_4^{20}$	$n_D^{\text{B}}$	$R_D$
0.00152	1.59255	1.4610	69.9
0.00269	1.59195	1.4616	70.1
0.00395	1.59132	1.4622	70.5 (69.7)

TABLE VI  
*p,p'*-TOLYL DISULFIDE  $M_w = 246.37$

<i>f</i>	$d_4^{20}$	$n_D^{\text{B}}$	$R_D$
0.00201	1.59301	1.4616	79.7
0.00500	1.59091	1.4632	80.0
0.00796	1.58854	1.4646	80.2
0.01190	1.58488	1.4664	80.4 (79.6)

TABLE VII  
*p,p'*-TOLYL TRISULFIDE  $M_w = 278.43$

<i>f</i>	$d_4^{20}$	$n_D^{\text{B}}$	$R_D$
0.00299	1.59195	1.4623	92.9
0.00423	1.59085	1.4629	93.4
0.00603	1.58895	1.4642	94.4
0.00794	1.58701	1.4654	94.9 (91.6)

TABLE VIII  
*p,p'*-TOLYL TETRASULFIDE  $M_w = 310.49$

<i>f</i>	$d_4^{20}$	$n_D^{20}$	$R_D$
0.00505	1.59012	1.4640	101.7
0.00792	1.58835	1.4662	101.8
0.00994	1.58665	1.4676	102.0 (101.2)

In the benzyl and tolyl polysulfides, the more sulfur atoms, the greater the molecular refraction becomes. The increase of refraction is about 9–10 per sulfur. For comparison with other polysulfides, molecular refraction and atomic refraction of  $S_n$  in *n*-hexadecyl polysulfide, ethyl polysulfide and methyl polysulfide are shown in Table X.

TABLE IX

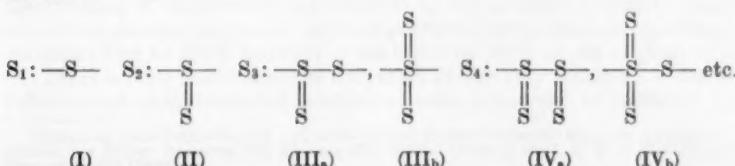
	Benzyl series		Tolyl series	
	Mol. refr.	Atomic refr. of $S_n$	Mol. refr.	Atomic refr. of $S_n$
Monosulfide —S—	70.5	10.0	69.7	9.2
Disulfide —S <sub>2</sub> —	81.3	20.8	79.6	19.1
Trisulfide —S <sub>3</sub> —	91.1	30.6	91.6	31.1
Tetrasulfide —S <sub>4</sub> —	100.2	39.7	101.2	40.7

The fact of the more sulfur atoms contained in a polysulfide the greater is the molecular refraction, amounting to 9–10 units per sulfur, shows the linearity of sulfur chain. Atomic refraction of thioketone sulfur had been reported as 7.2<sup>9</sup>. Strecker and Spitaler reported the atomic refractions of sulfur: S<sub>II</sub> = 7.80, S<sub>IV</sub> = 6.98 and S<sub>VII</sub> = 5.34 for two, four and six valency of sulfur, respectively.

TABLE X

	<i>n</i> -Hexadecyl poly-sulfide (C <sub>16</sub> H <sub>34</sub> ) <sub>n</sub> S <sub>n</sub>		Ethyl poly-sulfide (C <sub>2</sub> H <sub>5</sub> ) <sub>n</sub> S <sub>n</sub>		Methyl poly-sulfide (CH <sub>3</sub> ) <sub>n</sub> S <sub>n</sub>	
	Mol. refr.	Atomic refr. of S <sub>n</sub>	Mol. refr.	Atomic refr. of S <sub>n</sub>	Mol. refr.	Atomic refr. of S <sub>n</sub>
—S <sub>1</sub> —	158.41 <sup>6</sup>	8.43	28.52 <sup>5</sup>	7.85	—	—
—S <sub>2</sub> —	167.90 <sup>6</sup>	17.92	36.83 <sup>7</sup>	16.16	27.28 <sup>7</sup>	16.84
—S <sub>3</sub> —	176.50 <sup>6</sup>	27.06	47.48 <sup>6</sup>	26.81	35.96 <sup>7</sup>	25.52
—S <sub>4</sub> —	187.01 <sup>6</sup>	37.03	—	—	—	—

If the polysulfide is a type of thioketone the following structures may be considered:



The atomic refractions of these structures can be calculated by using the data as above<sup>9,10</sup>:

$$(II) = 14.2, \quad (III_a) = 21.4, \quad (III_b) = 19.7, \\ (IV_a) = 28.4, \quad (IV_b) = 26.9$$

These values are smaller than the found values. If we assume that sulfur is bonded linearly and calculate by using  $S_{11} = 7.80$ , the atomic refraction of  $-S_2-$  will be 15.6,  $-S_3-$  23.4 and  $-S_4-$  31.2. These values are smaller than those of the experimental data (Table IX). Supposing the structure to be thioketone, the differences are still smaller. This is because of small value of atomic refraction of two valent sulfur. The atomic refraction of sulfur is varied by the effects of both end radicals. This is clear from the present data and from the values by Woodron<sup>6</sup>. Therefore,  $S_{11}$  must be larger than 7.80, and the values of Strecker and Spitaler<sup>10</sup> should be recalculated.

### CONCLUSIONS

The molecular refraction of benzyl and tolyl polysulfide have been measured. The molecular refraction of benzyl and tolyl polysulfides increases with an increasing number of sulfur atoms by 9–10 units per sulfur atom.

From the fact of constancy of increase of molecular refraction per sulfur, the structure of polysulfides is considered to be linear.

### ACKNOWLEDGMENT

The author wishes to express thanks to Dr. H. Kambara for his helpful suggestions.

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# THE SEPARATION AND CHARACTERIZATION OF GRAFT COPOLYMERS FROM NATURAL RUBBER

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Graft copolymers formed by polymerizing vinyl monomers in the presence of natural rubber have been studied in some detail, both fundamentally<sup>1</sup> and technologically<sup>2,3</sup>.

Essentially the same interaction occurs whether polymerization is carried out in solution or in natural rubber latex.

The main interest has been with graft copolymers consisting of a rubber trunk chain of molecular weight about 200,000 with attached side chains of methyl methacrylate or styrene. These side chains have individual molecular weights<sup>1</sup> of 2000 to 5000, the proportions of vinyl polymer varying from 5–50% of the total. Properties of some of these copolymers are detailed, together with those of the corresponding homopolymers, in Tables I–III.

In solvents which dissolve both constituents they are in general freely soluble, but in a mixture of a good and a bad solvent they show novel colloidal properties which will be discussed in this paper.

## RUBBER-METHYL METHACRYLATE GRAFT COPOLYMERS IN SOLVENT MIXTURES AND IN A SINGLE PARTIAL SOLVENT

### GENERAL BEHAVIOR

Rubber of molecular weight  $10^6$ – $10^6$  is precipitated from a 1% solution in benzene by the addition of 20–22% methanol by volume, whereas polymethyl methacrylate of about the same molecular weight requires about 200%. In contrast the addition of methanol to a 1% solution in benzene of a typical graft copolymer causes no visible precipitation of any kind in the range in which the rubber trunk chain by itself would be precipitated. Addition of further methanol to just beyond 25% causes the formation of a slight turbidity which increases rapidly as more methanol is added, say up to 100%. The turbidity at this point is strong enough to make a 1 cm thickness of solution quite opaque. The sol is extraordinarily stable for long periods and over wide ranges of temperature and can be centrifuged at 3000 rpm without change. It has a characteristic brown translucency, while appearing white by reflected light. The addition of further methanol up to about 170% gives some increase in turbidity, and thereafter, in the absence of adventitious impurities or by the addition of minute quantities of calcium chloride, the turbid solution proves to have a sharp flocculation point corresponding to 183% addition of methanol to 100% of the original solution.

There is little doubt that the formation of this very stable sol is due to the rubber trunk chain becoming insoluble at some proportion of methanol (about

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5% calculated on the benzene) greater than where the rubber, if present in the free form, would have precipitated, and that the sol particles owe their stability to the still soluble methyl methacrylate graft side chains which presumably extend from the collapsed rubber nucleus. This behavior of the copolymer in mixed solvents provides a basis for separating it from the constituent homopolymers. Before this method could be considered reliable the effects of the various parameters on such separations had to be determined.

#### THE LIMITS OF PRECIPITATION OF THE SOL

*Dependence on relative amounts of constituents and their molecular weights.*—The initial turbidity point: The series of copolymers RM 1-8 detailed in Table I all showed their initial turbidity at an addition of 3-5% methanol after the precipitation point of free rubber as given above. This shows that the insolubilization of the rubber chain is retarded by the vinyl polymer part of the molecule but, above a certain minimum, is relatively unaffected by the amount attached. The degree of stabilization effected by only 5% methyl methacrylate

TABLE I  
GRAFT COPOLYMERS, RUBBER-METHYL METHACRYLATE SYSTEM  
COMPOSITION AND MOLECULAR WEIGHT

Polymer	Methyl methacrylate		Rubber M.W. $\times 10^{-4}$
	%	M.W. $\times 10^{-4}$	
RM 1	6	12	200
2	9	20	220
3	17	50	240
4	23	66	230
5	23	80	260
6	30	100	330
7	33	97	200
8	13	11	75

is quite remarkable, and usually allows degraded free rubber, if present, to be centrifuged from the sol produced in the initial stages of the precipitation. Due to the small amount of methanol needed to produce the initial turbidity, this is little affected by other factors such as temperature or concentration.

The sol flocculation point: As mentioned above, the rubber-methyl methacrylate sol requires the presence of a small amount of ionic material to cause flocculation. The amount required experimentally is about 0.00005%  $\text{Ca}^{++}$  which corresponds to roughly one ion per macromolecule. This is reasonable, since the gradual precipitation of the rubber trunk chain and later the methyl methacrylate graft chains from a 1% solution could result in a sol with particles consisting of single macromolecules. However, the appearance of such a marked turbidity showing simple reflection with white light suggests that the sol particles are considerably greater in size than this and hence that still less ionic material might be sufficient. Separations were normally effected using a 0.01% solution of calcium chloride in methanol, and under these conditions compounds prepared from controlled polymerizations gave sols which flocculated at  $183 \pm 2\%$  addition of methanol at 20° C. This figure does not vary as the amount of attached methyl methacrylate is increased from 5 to 30% on the rubber in compounds RM 1-7. A copolymer of similar constitution, but prepared in more dilute solution resulting in a rubber trunk chain of 75,000, and with total side chains of 11,000 molecular weight (RM 8) gave the same

flocculation point. Hence the flocculation point is essentially independent of the number of attached vinyl polymer chains, and also of length of rubber trunk chain.

By comparison, polymethyl methacrylate (M1) prepared in solution and having a molecular weight 690,000 gives a first visible precipitation (turbidity) point at 193% methanol, and one of molecular weight 330,000 (M2) at 197% (Table II). Hence the sol flocculation point of the graft copolymer always occurs before the first precipitation point of homopolymeric methyl methacrylates even if they have greater molecular weights than that of the whole compound molecule. The rubber part of the latter is evidently reducing the effective solubility of the whole compound.

*The effect of temperature.*—This is particularly interesting inasmuch as it should differentiate these solution-stabilized sols from ordinary sols of the charged particle type. In our case, the sol flocculation point should parallel, but be separate from, the precipitation point of the free homopolymer. This was found experimentally, the sol flocculation point of the compound RM-5 at

TABLE II  
RUBBER-METHYL METHACRYLATE SYSTEM. PROPERTIES OF  
SELECTED COPOLYMERS AND HOMOPOLYMERS

Polymer	Total M.W. $\times 10^{-3}$	Sol flocculation point or first turbidity point (% Methanol addition)			
		Standard concentrations	50° C	20° C	20° C
Copolymer RM 5	340	183 ± 1	285	—	135
Polymethyl methacrylate					
M 1	690	193	—	208	140
2	330	197	303	218	148
3	740				
Rubber					
R 1	480				

N.B. Standard concentrations: 1% polymer in benzene solution; 0.01%  $\text{CaCl}_2$  in methanol.

50° C requiring 285% addition of methanol while the homopolymer M2 required 303%. The difference is almost the same as that at 20° C, in accord with the theory that the stability reflects the solubility of the grafted chains as modified by the presence of the (collapsed) rubber trunk chain.

*The concentration of polymer.*—The sol flocculation point should not be greatly altered by altering the concentration, as was confirmed by experiment. With the homopolymers, however, the first appearance of turbidity prior to precipitation occurs sooner at the higher concentrations because the threshold value which can just be observed is reached sooner. The broader the molecular weight distribution, the more obvious is the effect. Thus polymethyl methacrylate of molecular weight 690,000 (M1) shows a first turbidity at 208% methanol in 0.1% solution instead of 193% in 1% solution, the corresponding figures for a molecular weight of 330,000 (M2) being 218% and 197%. Hence a more definite separation is possible in the more dilute solutions.

*The effect of ionic substances.*—The sol flocculation point is independent of calcium chloride concentration between 0.00005% and 0.02% on the methanol. Above this concentration, however, both the rubber-methyl methacrylate compound and free polymethyl methacrylate are affected. This effect is not well

known and is worthy of notice because it serves to increase the precipitating power of the methanol and can sometimes be used to flocculate a copolymer sol which is otherwise stable in a given solvent mixture. In the methacrylate system, the amount of methanol required to flocculate a typical compound sol is decreased from 183% to 135% by addition of 1% calcium chloride to the methanol. Similar changes in the first precipitation points for the homopolymers of molecular weight 690,000 and 330,000 are 193% to 140% and 197% to 148%. The decrease in solubility, therefore, affects both copolymers and homopolymers to roughly equal extent, and is formally analogous to a "salting out" effect.

#### BEHAVIOR IN SINGLE PARTIAL SOLVENTS

It is clear that the solubility characteristics of the rubber-methyl methacrylate graft copolymers conform to a pattern whereby the methyl methacrylate increases the solubility limits of the rubber and the rubber decreases those of the methyl methacrylate, the stability of sols formed in mixed solvents depending on the solubility and Brownian movement of that part of the molecule still solvated. This behavior is paralleled in single partial solvents which dissolve only one of the constituent homopolymers. Thus acetone, in which rubber is insoluble and polymethyl methacrylate freely soluble, will slowly peptize solid graft copolymers directly into sols. More readily, flocculated sols separated by decantation from benzene-methanol mixtures can be redispersed by adding acetone and gently stirring. Such sols have all the properties previously described. This reinforces the view that the stability of the sol is a simple solubility effect and not for example due to any partition of the mixed solvents between the two constituents of the copolymer.

#### RUBBER-STYRENE GRAFT COPOLYMERS

Having demonstrated the principles underlying the solubility characteristics of the rubber-methyl methacrylate graft copolymers, these can be extended to other combinations, e.g., to similar graft copolymers from rubber and styrene<sup>1</sup>.

Rubber and polystyrene have similar solubilities in benzene-methanol mixtures and titration of rubber-styrene compounds in the presence of the free polymers therefore causes practically continuous precipitation. According to the above considerations, the addition of substance which is a solvent for styrene, but not for rubber, should improve the resolving powers of the solvent-precipitant mixture. In fact, substitution of a 2/1 methylethylketone/benzene mixture for pure benzene gives selective precipitation very similar to that described for the methyl methacrylate system. The first turbidity point of the compound is about 5% methanol and the sol flocculation point about 20%. These values also show the same relation to the precipitation points of the free homopolymers as did the previous system, but an important difference is that the stability of the rubber-styrene sols is far less and no ionic material is needed to flocculate them. This relative instability is used to advantage in the semi-quantitative separation involving successive additions of methanol to a polymerization mixture containing (residual) rubber, rubber-styrene graft copolymer and free polystyrene and illustrated in Figure 1. The incidence of turbidity was noted and then the sol was centrifuged clear at 3500 rpm and the volume of precipitate measured. The additive curve gives the total volume of precipitate while the differential curve has been derived from it in the usual way.

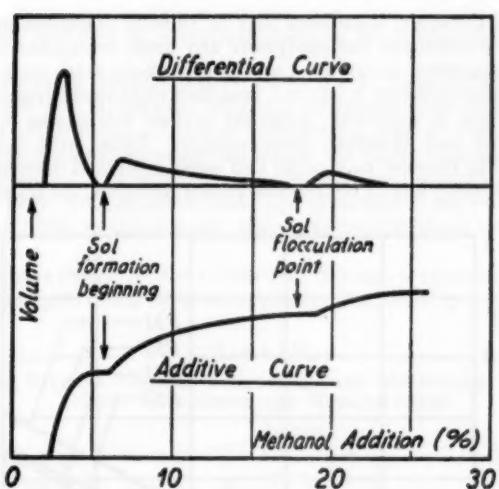


FIG. 1.—Fractional separation of rubber-styrene compound from free rubber and free polystyrene.

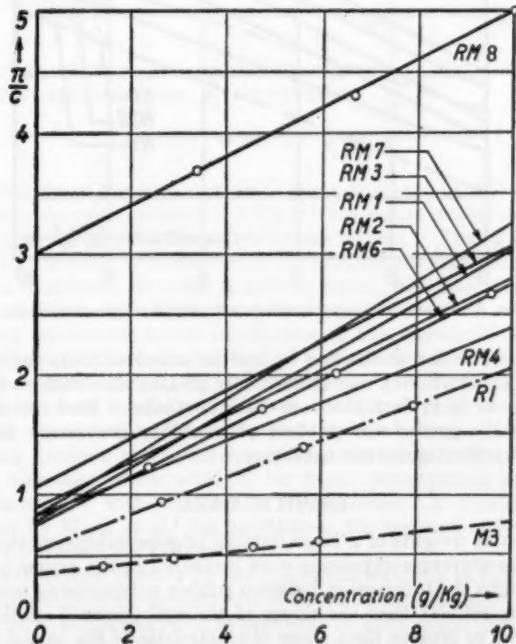


FIG. 2.—Osmotic molecular weight data for rubber-methyl methacrylate compounds.

In general, therefore, it appears that by suitable consideration of the solubilities of the constituent homopolymers any graft copolymer of this general type can be separately isolated. Certain exceptions arise, such as where the more soluble homopolymer exists in a branched state in the free form with consequent reduction in solubility, while the grafted side chains of this material are unbranched and therefore more soluble. Thus, with acrylates where branching due to transfer may occur and cause a marked decrease in the solubility of the polyacrylate in benzene-methanol mixtures, the separation is more

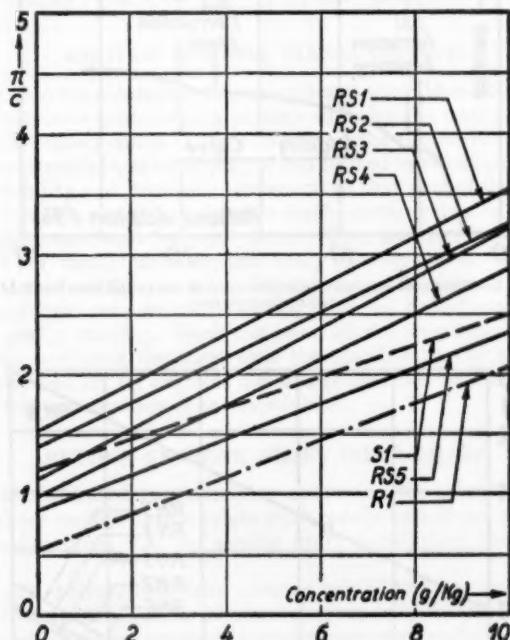


FIG. 3.—Osmotic molecular weight data for rubber-styrene compounds.

difficult. Recourse can sometimes be had to mixed solvents such as benzene-ketone mixtures which may confer markedly greater solubility on the branched homopolymer, as is in fact the case with acrylates. Such mixtures do not follow the readily predictable pattern of solubility previously described and such day-to-day strategems are necessary.

#### OSMOTIC DATA

The molecular weights of a large number of pure rubber-methyl methacrylate and rubber-styrene compounds were measured in the course of the kinetic investigation into the interaction between rubber polymerizing monomers<sup>1</sup> and it soon became evident that the slopes of the  $\pi/C$  versus  $C$  relationships were always equal to or greater than those characteristic of the initial rubber or of rubber of similar molecular weight to the trunk chain. The osmotic determina-

tions otherwise provided no abnormal features, the relationship  $\pi/C$  versus  $C$  being linear.

Figure 2 shows the osmotic data for the series of rubber-methyl methacrylate compounds RM 1-8 in benzene (M3 is a polymethyl methacrylate prepared under similar conditions). There is considerable scatter but considering the amount of manipulation necessary to isolate the pure compounds the consistency is satisfactory. The determinations were mostly made in Zimm-Myerson osmometers, a few, such as RM6, being also measured in the Fuoss-Mead type. The fact that RM8, of much lower molecular weight, gives the same slope is noteworthy.

Figure 3 shows results for the rubber-polystyrene compounds RS 1-6 (Table III), the slopes again being equal to or greater than those given by the original rubber.

TABLE III  
RUBBER-STYRENE SYSTEM. COMPOSITION AND MOLECULAR WEIGHT:  
GRAFT COPOLYMERS AND HOMOPOLYMERS

Copolymer	Styrene		Rubber M.W. $\times 10^{-4}$
	%	M.W. $\times 10^{-4}$	
RS 1	3	5	164
2	9	16	168
3	13	30	197
4	17	43	218
5	19	57	247
Polystyrene			
S 1		230	—

The relation between the osmotic pressure  $\pi$  and the concentration  $c$  is given, to a first approximation, by the equation

$$\pi/C = RT/M + BC$$

where  $B$ , the slope of the  $\pi/C$  versus  $C$  curve is given<sup>4</sup> by  $RT/(0.50-\mu)/V_1d_2^2$ .  $\mu$  is a semiempirical constant related to the solvent-solute interaction and hence to the solubility of the polymer in any particular solvent. Thus if a given solvent is modified by addition of non-solvent, the  $\mu$ -value increases until, when phase separation is imminent, its value is approximately 0.50 and the  $\pi/C$  versus  $C$  curves are parallel to the abscissa<sup>5</sup>.

The effect on solvent-solute interaction of the introduction of branching points into linear polymers has previously been studied for vinyl polymers and for rubber in rather different ways. Thus Doty et al.<sup>6</sup> have shown that the introduction of a very small amount of crosslinking in polystyrene, insufficient to give phase separation, causes a marked increase in the  $\mu$ -value indicating a corresponding decrease in the solvent-solute interaction. This necessitated a substantial correction when  $\mu$ -values for linear polystyrenes were applied to swelling experiments with crosslinked polystyrenes. A similar change in  $\mu$  was observed by Mark et al.<sup>7</sup> for polyethenes, the amount of branching being determined from the  $\text{CH}_3/\text{CH}_2$  ratio.

In contrast, extensive work on the equilibrium swelling of lightly crosslinked rubber has shown that the solvent-solute interaction parameter involved in this case has the same numerical value as that derived from vapor pressure or osmotic determinations on unmodified rubber<sup>8</sup>. Hence it appears that for rubber the  $\mu$ -value for the linear chains is not altered by the introduction of tetrafunctional

branching points over the range of  $M_e$  (the molecular weight between cross-links) studied.

Our experiments, showing that the same  $\mu$ -values are obtained from osmotic determinations on graft copolymers of rubber as with rubber itself, are therefore in line with the latter assumption, while the absence of such effects as Doty observed indicates in addition that the individual short vinyl side chains do not enter into the solvent-solute interaction to any great extent. (The values of  $M_b$ , the molecular weight between branch chains, lie in the same range as the values of  $M_e$  for the crosslinked rubber.)

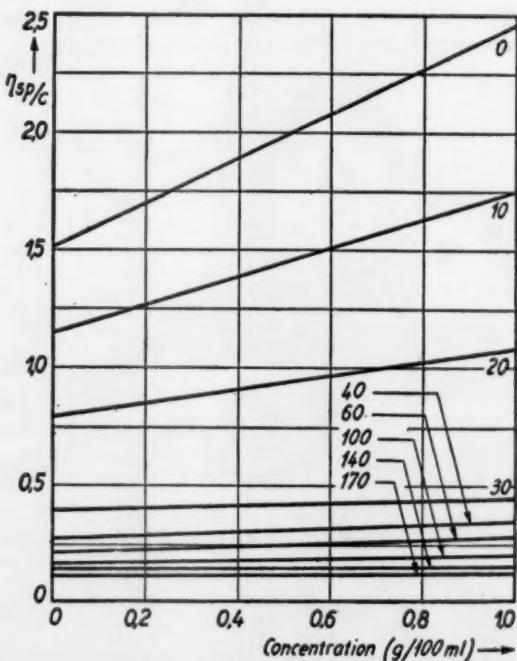


FIG. 4.—Reduced viscosity-concentration curves for a rubber-methyl methacrylate compound; the percentage addition of methanol to 100 parts benzene being shown adjacent to each curve. Graft polymer containing 15% bound methyl methacrylate (from a technological preparation in latex).

#### VISCOMETRIC AND TURBIDIMETRIC DATA

Simple determinations of intrinsic viscosities do not reveal any clear differences between the compounds and plain mixtures of rubber and methyl methacrylate so that the main interest again lies in the behavior in mixed solvents.

In order to follow the collapse of the rubber trunk chain, intrinsic viscosities were studied in benzene-methanol mixtures corresponding to the complete range of solubility of the compounds.

Some  $\eta_{sp}/C$  curves are shown in Figure 4 and the intrinsic viscosities are plotted in Figure 5 (lower part) against the per cent methanol addition. The line parallel to the ordinate at 22% addition indicates the approximate point at

which the rubber trunk chain would precipitate (as a swollen gel) if it were present as free rubber. The intrinsic viscosity is reduced proportionately to the amount of methanol added, this relation continuing just past the point at which turbidity appears. The intrinsic viscosity then decreases steadily at a much reduced rate presumably due to collapse of the methyl methacrylate side chains and to further reduced solvation of the rubber trunk chain.

The progress of collapse of the rubber trunk chains has also been followed for the same copolymer by measurements of the turbidity of the sol using a Spekker photo-absorptiometer. The graft sols give a linear relation between

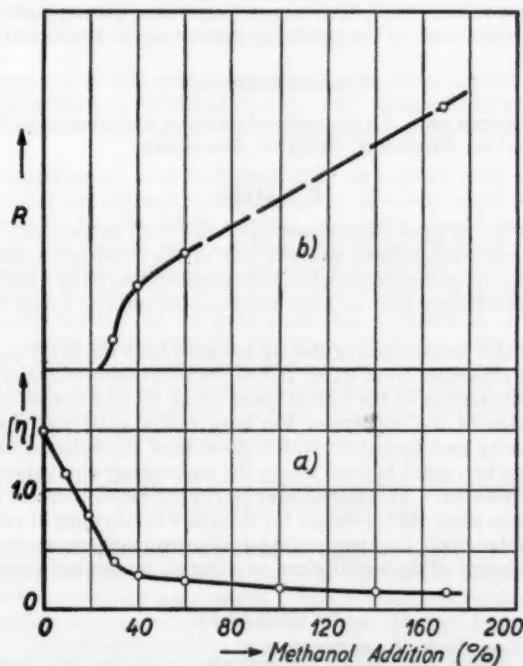


FIG. 5.—Variation of intrinsic viscosity (a) and turbidity (b) with composition of solvent (expressed as % methanol addition to 100 parts benzene).

the dial reading  $R$  and the concentration of total polymer. Above  $R = 1$  there is a slight falling-off in linearity which also occurs, for example, with barium sulfate suspensions.

The turbidity at constant polymer concentration increases rapidly in the first stages of methanol addition and then more gradually (Figure 5, upper part).

#### CONCLUSIONS

The solubility of graft copolymers prepared from rubber and vinyl monomers follows a general pattern whereby one of the constituents can be insolubilized while the other remains soluble, the compound forming a stable sol which is

largely unaffected by heat or ionic materials at suitable ratios of solvent to precipitant. The onset and flocculation of the sol are such that the graft copolymer can be completely separated from either free constituent homopolymer.

This insolubilization of the rubber trunk chain by addition of methanol to a benzene solution of the copolymer has been followed by the changes in the intrinsic viscosity and turbidity, which show that the collapse of the rubber chain continues to a point beyond where the molecularly equivalent free rubber would be precipitated. This period also marks the major increase in turbidity.

Osmotic data show that  $\mu$ -values for the grafted copolymers of rubber are the same as for rubber itself, thus supporting similar assumptions made in the application of the theory of the equilibrium swelling of crosslinked rubber.

#### ACKNOWLEDGMENT

This work forms part of a program of research undertaken by the Board of the British Rubber Producers' Research Association.

#### SUMMARY

The solubility of graft copolymers prepared from rubber and vinyl monomers follows a general pattern whereby one of the constituents can be insolubilized while the other remains soluble, the compound forming a stable sol which is largely unaffected by heat or ionic materials at suitable ratios of solvent to precipitant.

The onset and flocculation of the sol are such that the graft copolymer can be completely separated from either free constituent homopolymer.

This insolubilization of the rubber trunk chain by addition of methanol to a benzene solution of the copolymer has been followed by the changes in the intrinsic viscosity and turbidity, which show that the collapse of the rubber chain continues to a point beyond where the molecularly equivalent free rubber would be precipitated. This period also marks the major increase in turbidity.

Osmotic data show that  $\mu$ -values for the graft copolymers of rubber are the same as for rubber itself, thus supporting similar assumptions made in the application of the theory of the equilibrium swelling of crosslinked rubber.

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# GRAFT POLYMERS WITH PRESET MOLECULAR CONFIGURATIONS \*

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## INTRODUCTION

The concept of "tailor-made" macromolecules when applied to graft polymers implies an effective correlation between the chemical and physical properties of the component parts and the technological properties of the resultant whole.

Earlier experiments<sup>1</sup> have indicated that, for a given graft macromolecule of natural rubber and polymethyl methacrylate, one extreme physical configuration could readily be effected in solution, viz., with the rubber trunk chains collapsed and the methyl methacrylate side chains extended. The complementary configuration—rubber chains extended and the methyl methacrylate chains collapsed—seemed equally easy of achievement. If these configurations could be carried through to the solid state then comparison of the properties of the dry rubbers would provide one such correlation between established physical configurations and resultant technological properties.

The evidence for these definite configurations is briefly described below followed by preparative methods for bulk quantities of the dry rubbers and the evaluation of their technological properties.

## CONFIGURATION OF GRAFT POLYMERS IN SOLVENT-PRECIPITANT MIXTURES

When rubber-methyl methacrylate graft polymer—prepared in solution<sup>1,2</sup> or on a commercial scale from rubber latex<sup>3,4</sup>—is dissolved in benzene, both chains are extended to a relatively large extent. This is confirmed by the large solvent-solute interaction, corresponding to small  $\mu$  values, obtained from osmotic measurements<sup>5,6</sup>. If methanol is added in a proportion normally sufficient to precipitate free rubber, a white colloidal "sol" is formed, the rubber chains having collapsed to give colloidal particles which are stabilized by the still soluble methyl methacrylate side chains. This collapse of the rubber trunk chains was substantiated by following viscosity changes of solutions of the order of 1% of the graft polymer in benzene as successive additions of methanol were made.

The resultant intrinsic viscosities are shown as a function of the composition<sup>2</sup> of the "solvent" in Figure 1, the line XY indicating the percentage methanol required to precipitate free rubber as a swollen mass. The first portion AB shows the initial coiling of the rubber trunk chain as the precipitant, methanol, is added. Approximately at the point B the solution becomes strongly turbid, indicating that the chains of rubber, which would precipitate were they not attached to soluble methyl methacrylate chains, are sufficiently collapsed to

\* Reprinted from the *Journal of Polymer Science*, Vol. 24, pages 467-477 (1957). The author's present address is Fisons Limited, Harvest House, Felizatow, England.

give Tyndall scattering of the incident light. Subsequent addition of methanol reduces the swelling of the colloidal particles of rubber, thus lowering the viscosity still farther. The effect ceases at C, which therefore indicates the limit of collapse of the rubber chains. The chains of polymethyl methacrylate over the initial stages extend slightly until about 25% methanol addition and then contract as shown by intrinsic viscosities measured similarly for pure polymethyl methacrylate<sup>5</sup>. The observed line ABC is therefore the resultant of the individual changes in the coiling of the rubber and methyl methacrylate parts of the molecule. The small decrease in viscosity after C is presumably due to further slight coiling of the methyl methacrylate chains, precipitation of polymethyl methacrylate requiring about 200% methanol addition.

Such experiments cannot prove whether the particles of the colloidal solution consist of individual collapsed chains or clusters of such chains, i.e., micelles, but the latter state is more likely since, if sufficient rubber chains are associated, the extent of coiling required for each individual chain would be reduced. Such an association would account for the pronounced turbidity. There would

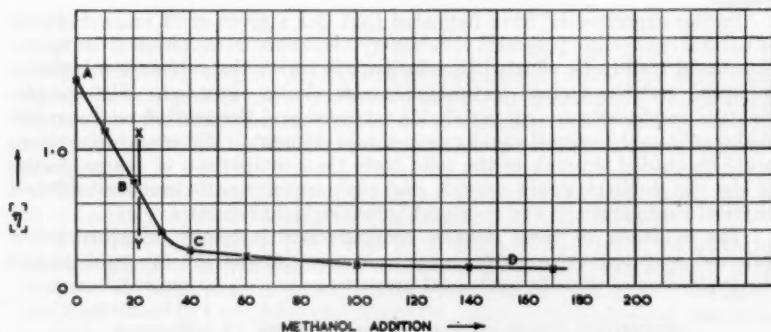


FIG. 1.—Viscosity dependence on solvent/precipitant ratio.

seem to be a limit to the number of chains per micelle since the attached methyl methacrylate chains in extended form would hinder the aggregation of unlimited numbers of collapsed chains. The very high stability of these colloidal solutions over many months indicates little tendency to aggregation beyond the initial level.

In the present paper "gross" graft polymers consisting of free rubber and free polymethyl methacrylate as well as grafted molecules of rubber combined with methyl methacrylate were used, but similar effects occur with the grafts themselves from which the free polymethyl methacrylate has been separated. In view of the marked solubilization of free rubber by the graft molecule<sup>6</sup>, the free rubber and free methyl methacrylate are most probably closely associated with the corresponding parts of the graft molecule.

These experiments strongly suggest that after the first main decrease in viscosity the graft polymer is in one of the required extreme configurations, viz., with the rubber chains collapsed and the methyl methacrylate chains extended. By analogy the turbidity produced by adding petroleum ether (in which methyl methacrylate is insoluble) to a benzene solution of the copolymer is caused by collapse of the methyl methacrylate side chains, the rubber chains now providing the stable factor.

## EXPERIMENTAL

## HIGH SOLIDS COLLOIDAL SUSPENSIONS OF GRAFT POLYMERS

The above experiments, made at or below 1% solids concentration, have been extended to the preparation of high solids suspensions of commercial graft polymers. Thus Heveaplus MG30<sup>7</sup> containing 30% methyl methacrylate and 70% natural rubber with about half of the rubber and of the methyl methacrylate present as free polymer and the rest consisting of graft polymer has been used extensively. The chain lengths of the free polymer, free rubber, and component chains of the graft are roughly of the same order, i.e., in the range 200,000 to 500,000 molecular weight<sup>8</sup>. Experiments using benzene/petroleum ether to give complementary configurations were also made. Typical preparations are listed in Table I.

The mixes in the initial stages are gels which, after about half the precipitant has been added, change quite rapidly to free flowing turbid fluids. Since the majority of the graft material is rubber, which is also inherently more viscous, *A* shows a much greater reduction in viscosity than *B*. The free flowing nature of these suspensions is illustrated in Figure 2 (top).

TABLE I

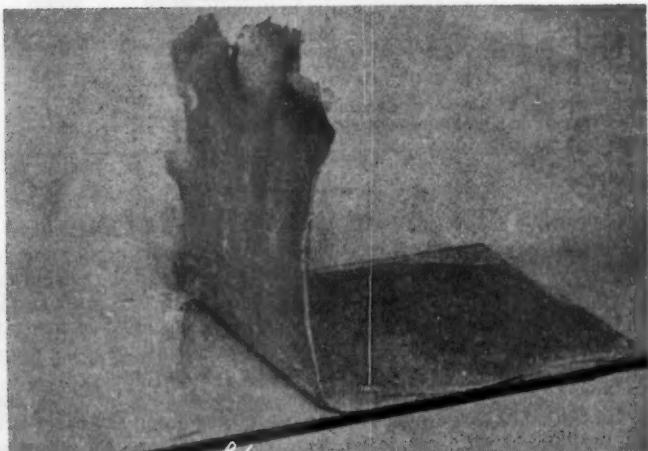
	<i>Form A</i>	<i>Form B</i>
Rubber chains collapsed	Rubber chains extended	
Methyl methacrylate chains extended	Methyl methacrylate chains collapsed	
Heveaplus MG30	40	40
Benzene	40	35
Left to swell overnight in a covered Z-blade mixer and then mixed for 20 minutes followed by the slow addition of:		
Methanol	20	—
Petroleum ether	—	25

These high solids suspensions with the rubber chains collapsed have been called "solvent latexes" because they consist of the insoluble rubber part of the graft molecule stabilized as a colloid particle by the action of the solvent on the other part of the molecule, thus resembling the particles of a latex stabilized by proteins or soaps, and because they can be prepared in similar concentrations to those of natural rubber latexes. The highest concentrations so far prepared—about 60% solids—have been used for "knifing" on to fabric.

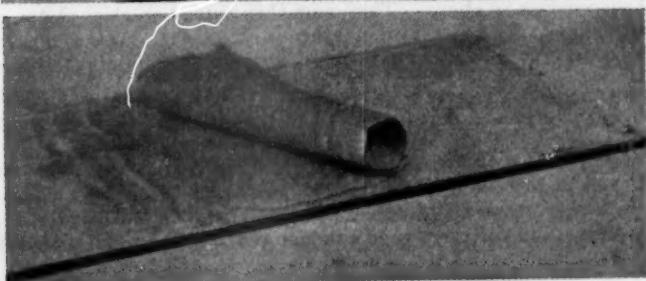
For technological tests, the solid MG30 was compounded for vulcanization and this bulk split into three portions, one for a control and the other two for the preset configurations. The latter were converted into the appropriate colloidal suspensions as above. They were then spread on glass plates, partially dried, stripped, dried first in air and then *in vacuo* at 30–35°C to remove the last traces of solvent, and cured in sheets to give the appropriate testpieces.

## PROPERTIES OF THE SOLID POLYMERS WITH PRESET CONFIGURATIONS

The two forms, *A*, rubber chains collapsed, methyl methacrylate chains extended, and *B*, rubber chains extended, methyl methacrylate chains collapsed, show very marked differences (Figure 2). *A* is hard and stiff with nontacky surface and with very good adhesion to the glass surface on which the



(A)



(B)

FIG. 2.—Properties of high solids suspensions and resultant dry rubbers.

original colloidal suspension was spread for drying. *B* is soft and flabby, and, although self-adherent, strips very readily from a glass surface. Thus the "hard" form *A* shows predominantly the properties of the rigid modifying plastic polymethyl methacrylate, while the "soft" form *B* shows mainly rubbery characteristics. The properties of the original material (Heveaplus MG30) are intermediate.

These differences followed prediction sufficiently closely to warrant a quantitative determination of tensile strength, elongation-at-break, hardness, modulus at 100 and 300% elongation, tear at 20, 80, and 120° C. The results are shown in Table II.

TABLE II  
TENSILE AND STIFFNESS PROPERTIES OF MODIFIED RUBBERS

Form	Cure, min/temp.	T.S., kg/cm <sup>2</sup>	E.B., %	M100, M300,		Hard- ness, BS <sup>o</sup>	Tear, kg/mm.		
				kg/cm <sup>2</sup>	kg/cm <sup>2</sup>		20°	80°	120° C
Hard <i>A</i>	20/140° C	200	355	64	177	86	0.54	0.79	0.57
	30	187	345	66	168	85			
	40	132	260	68	—	86			
Soft <i>B</i>	20/140° C	297	500	15	142	59	0.12	0.22	0.18
	30	280	485	20	148	62			
	40	282	475	19	150	62			
Original as prepared	20/140° C	256	460	48	144	82	1.40	1.25	0.38
	30	278	485	48	148	82			
	40	265	475	47	146	85			
<i>After Heavy Milling</i>									
Hard <i>A</i>	30/140° C	171	375	50	130	84			
Soft <i>B</i>	30/140° C	260	480	28	132	68			
<i>"Cold" Curing</i>									
Hard <i>A</i>	300/60° C	73	220	35	—	67			
Soft <i>B</i>	300/60° C	211	490	16	87	56			
Original	300/60° C	175	560	13	47	56			

T.S. = tensile strength, E.B. = elongation at break, M100 = "Modulus" at 100% elongation, M300 = "modulus" at 300% elongation.

These properties and the tear strength are measured by the standard methods described in BPRRA publications.

*Elastic properties.*—The optimum values correspond mainly with 30 minute cures. Ignoring minor differences, the soft form *B* gives maximum tensile and elongation at break, while the hard form *A* gives maximum modulus (i.e., stiffness) at 100 and 300% elongation and also maximum hardness. Comparisons with the results for the original Heveaplus shows that *in this particular case* the material as prepared gives nearly optimum properties.

Heveaplus grafts as prepared and normally compounded show modulus reinforcement (i.e., increase in stiffness without decrease in tensile strength) only provided the material is heated above the second-order transition point of the methyl methacrylate (i.e., over 100° C) before, during or after cure<sup>8</sup>. This effect is unconnected with the actual vulcanizing or crosslinking, being shown by the raw material. By analogy with the above results, it can probably be associated with a methyl methacrylate structure. This stiffening is reversible since milling gives the soft form which is again hardened by heating etc. *ad infinitum*, so that the structure responsible for reinforcement is metastable with respect to shearing and temperature.

By contrast, it is of great interest that both hard and soft preset forms are stable to temperature and shear. The hard form, if anything, is rendered harder and the soft form softer by heating to 140° C and then cooling to room temperature. Under very heavy milling these two forms show a slight variation in properties towards the mean, but both are effectively stable (Table II). It seems, therefore, that the preset configurations represent stable states.

The necessity for heating to produce reinforcement in the material as originally prepared should not be required with the hard form if a methyl methacrylate structure is already present. This is confirmed by "cold" curing at 60° C (below the second-order transition point of the methyl methacrylate) using Butyl 8 as an accelerator (manufactured by R. T. Vanderbilt Co., Inc.). The results (Table II) show that the stiffness at 100% extension (M100) of the hard form is more than double that of either the original or the soft form.

*Cyclic stress-strain behavior.*—The apparently different modulus behavior of the hard and soft forms after normal high temperature vulcanization at 100 and 300% elongation is explained by the cyclic stress-strain data of Figure 3. The characteristic shape of the equilibrium form of the hysteresis curves is shown

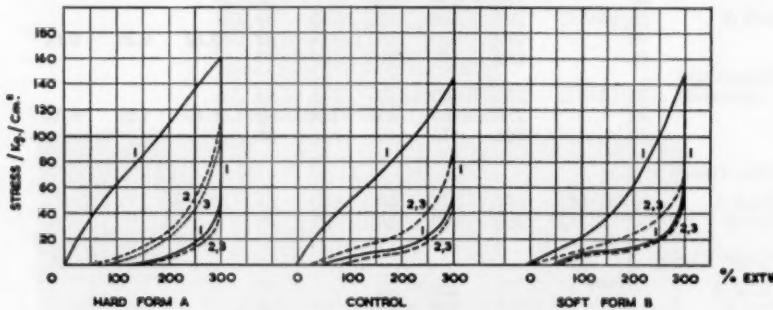


FIG. 3.—Cyclic stress-strain measurements.

for all three forms by the second and third loops which have low 100% and high 300% modulus values, i.e., they are concave upward. The soft form shows initially a relatively low M100 value consistent with this. By contrast, the hard form shows high initial values at 100% elongation, indicating a structure which later breaks down. (It is surprising that milling before vulcanization does not reduce the M100 values proportionately more than the M300 values.)

The Heveaplus MG30, compounded as prepared, shows an initial shape closely similar to the hard form but with a slight concavity at about 200% elongation, thus resulting in a somewhat lower M300 value.

*Tear strength.*—The results detailed in Table II show that, whereas the soft form B gives very poor tear strength, irrespective of temperature, the hard form A gives moderately good tear strength, again independent of temperature. It was particularly noteworthy that the hard form exhibited "knotty" tearing even above the second-order transition point of the polymethyl methacrylate.

## DISCUSSION

Treating the collapsed or extended polymer chains as extreme physical configurations for the component parts of graft polymers, the results indicate that

(1) For a given chemical configuration, e.g., for a particular type of graft copolymers, different physical configurations can confer widely different over-all mechanical properties.

(2) Where the polymeric component forming the extended phase is rigid (glasslike), the stiffness of the total copolymer at normal temperatures is greatly enhanced as shown by modulus and hardness measurements. Where the rigid component forms the discontinuous phase there is no modulus reinforcement or increased hardness.

(3) The over-all mechanical properties of dry rubbers containing graft polymers are not necessarily dominated by the component forming the extended phase. As expected, the presence as the extended phase of a polymeric component with a definite second-order softening (transition) point, e.g., methyl methacrylate, results in complete loss at elevated temperatures of the modulus reinforcement which is conferred at lower temperatures. By contrast, tear strength is independent of temperature and the highest values recorded are where the polymethyl methacrylate is the extended phase. Hence these high values must be attributed to the discontinuous (rubber) phase. This was unexpected, although an indication had previously been given in experiments by P. McL. Swift in these laboratories when he showed that methyl methacrylate modified rubber could be prepared with good hot tear strength by varying arbitrarily the method of preparation.

The exact structure of graft polymers in the types of preset configurations discussed cannot at present be completely defined. It seems probable that the insoluble particles of the original dilute colloidal solution each consist of a number of collapsed chains. This micelle formation is more likely since each individual chain will be less tightly coiled. Also the marked turbidity of the colloidal solutions corresponds to a particle size greater than would be expected from a single collapsed polymer chain.

The same configuration and type of aggregation would be expected in the high solids suspensions and, provided the solvent/precipitant ratio remained the same, should be carried through to the dry rubber. There is a further and probably more potent reason why this latter should be so.

It is known that, in general, two high polymers are mutually compatible with one another only if their free energy of interaction is favorable, i.e., negative<sup>9</sup>. This is very rarely so since the entropy to be gained by mixing relatively small numbers of large molecules is small and can readily be counteracted by a small positive heat of mixing. Since the mixing of a pair of polymers, or of pairs of solutions of different polymers, is usually endothermic, incompatibility of polymers normally occurs, in the latter case resulting in visible separation into two phases, each containing one polymer only. This effect, which can be considered as a simple repulsion between unlike long chain molecules, has been clearly demonstrated for, *inter alia*, rubber and polystyrene<sup>10</sup>. This repulsive effect also shows itself when long chains of different polymers are chemically linked (as in graft polymers) when the molecule in solution is extended, resulting in a greater solvent-solute interaction as shown by the slope of the reduced osmotic pressure-concentration curves<sup>2</sup>.

Where, therefore, separation of the two components of a graft polymer has been induced by solvent/precipitant action, this will be stabilized by the repulsive effect. Also, as will be shown later, simple solution of a graft polymer may be sufficient to allow a marked degree of separation as revealed by the mechanical properties of the dry polymer before and after solution.

The same considerations apply to both the extremes we have been considering. Microseparation to give either component chain collapsed will represent negative free energies of interaction and, once formed, any attempt to obtain homogeneity would involve a positive free energy change which would be improbable. Either extreme configuration will be more stable than the intermediate (metastable) form, and conditions will determine which in fact is formed.

If the colloidal particles being considered are, in fact, micelles, then they presumably consist of a nucleus of collapsed chains of the one component surrounded by extended chains of the other component. When the solvent-precipitant is evaporated, the swollen and then the dry polymer should consist of the domains of the collapsed chains as a discrete phase in a continuous phase of the extended chains. This applies to either extreme configuration. Any free rubber or polymethyl methacrylate present is presumably associated with the like part of the graft<sup>6</sup>.

This microseparation into two phases will be stabilized by the free energy considerations already advanced. Further separation will be unlikely because the two component chains are chemically bound together. This will tend to give a fairly definite "interface" between the two types of polymer chains. Heating above the "melting" point of the rigid polymer will tend only to further clarification or condensation of the same sort and will not markedly alter the relative sizes of the two domains. A similar explanation accounts for the stability to heavy shear demonstrated above. By extensions of this reasoning, if a graft polymer with both types of chain extended were milled with say 10% of a plasticizer-solvent favoring collapse of one form and extension of the other, then each time the polymer chains were distorted into a configuration favored by the free energy considerations they would stay put, and each time they were distorted into an unfavorable configuration they would endeavor to revert to their former state. Thus each component of the graft would gradually take up the favored form.

The further general conclusion can be drawn that the method of preparation, according as it tends to produce collapsed or extended chains, will have a profound, and in some cases predictable, effect on the mechanical properties of the resultant modified rubber. As an example, one can consider the production by the normal method<sup>4,7</sup> of methyl methacrylate and styrene modified latexes. The rubber latex particles are swollen with methyl methacrylate and styrene monomers, respectively. The former is a poor solvent for rubber and therefore tends to coil the rubber chains. As it polymerizes, the polymethyl methacrylate formed is soluble in the monomer and therefore tends to give extended chains. After polymerization is complete the modified rubber is obtained by coagulation and drying, and, as shown by the control results above, exhibits mainly the stiffness and hardness corresponding to a polymethyl methacrylate structure. By contrast, using styrene the rubber is readily soluble in the monomer and hence the rubber chains are extended before polymerization of the styrene starts, and the resultant modified dry rubber is much softer for the same content of synthetic polymer, although pure polystyrene is at least as hard and stiff as polymethyl methacrylate.

This profound effect of the solvent relative to the component parts of a graft polymer is strikingly demonstrated by dissolving in benzene the stiff Heveaplus MG as normally prepared, pouring on to a glass plate, and drying off again in the usual manner. The result is a soft film, very much resembling the rubber extended, polymethyl methacrylate collapsed, form. This is obviously due to the much greater extension of the rubber chains in benzene com-

pared with the polymethyl methacrylate chains, thus favoring the rubber extended form. This difference in extension of the two individual chains can be demonstrated by measuring the viscosities of rubber and polymethyl methacrylate in benzene and benzene + methanol. Rubber gives its greatest viscosity in pure benzene but polymethyl methacrylate in benzene + ca. 25% methanol<sup>6</sup>.

### SYNOPSIS

It has previously been shown that, when a graft polymer of rubber and polymethyl methacrylate is dissolved in benzene and a limited amount of methanol added, the hydrocarbon rubber chains collapse to form colloid particles stabilized by the still soluble polymethyl methacrylate chains. Similar high solids dispersions of this type and of the complementary type with the vinyl polymer chains collapsed have now been prepared and evaporated down to give dry modified rubbers. Due to the known incompatibility between different polymers the microseparation in the colloid suspension is carried through to the dry polymer. It is shown that the form with rubber chains collapsed, polymethyl methacrylate chains extended, is hard, shows modulus reinforcement, and adheres strongly to glass, while the form with polymethyl methacrylate chains collapsed, rubber chains extended, is soft, shows no modulus reinforcement, and does not adhere to glass. This indicates that the extended chains mainly govern these particular properties. On the other hand, good hot tear strength seems to be conferred by the *collapsed* rubber chains, the alternative form with extended rubber chains giving poor tear at all temperatures. The possibility of predicting the configuration and hence the mechanical properties given by any particular method of preparation is discussed and examples are given.

### ACKNOWLEDGMENT

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## CIS-1,4 POLYISOPRENE PREPARED WITH ALKYL ALUMINUM AND TITANIUM TETRACHLORIDE \*

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Recently, several reports on the preparation of polyisoprene of high *cis*-1,4 isomer content have appeared<sup>2,3,4</sup>. This essential duplication of natural rubber by two different catalyst systems is a major contribution to rubber research. The discovery assumes more importance in light of the predicted shortage of natural rubber by 1960. Because of the economic and military impact of synthetic *cis*-1,4 polyisoprene, it was believed important to evaluate all methods of its production. Consequently, in addition to developing *cis*-1,4 polyisoprene catalyzed by lithium, this laboratory has also evaluated the alkyl aluminum-titanium tetrachloride catalyst system.

K. Ziegler<sup>5</sup> has used this catalyst system for making low pressure polyethylene. The mole ratio specified in early Ziegler patents was 8 moles or more of triethyl aluminum to 1 of titanium tetrachloride. For polymerizing isoprene, this ratio was unsuccessful; however, when less triethyl aluminum was used, better results were obtained. In the work described here, the effect of catalyst composition, temperature of polymerization, and solvent upon the properties of the polyisoprene are explored.

### EXPERIMENTAL

Polymerization was usually done in a petroleum ether solution, using a 75-25 solvent-monomer mixture by volume. The monomer was Phillips Petroleum Co.'s isoprene (99 mole % pure), refluxed prior to use for 2 hours with sodium paste, and distilled. Petroleum ether, ACS grade, was purified by treating with concentrated sulfuric acid until no further discoloration developed, washed with water, dried by passing through an alumina column, and distilled from sodium paste to assure removal of the last traces of moisture.

Because of the reactivity of the catalyst components and for ease of handling, one molar solutions of alkyl aluminum and titanium tetrachloride were prepared in *n*-heptane purified by a sulfuric acid treatment similar to that used for petroleum ether. These solutions were stored in beverage bottles that had been previously baked at 110° C for several days to remove the adsorbed moisture. The titanium tetrachloride (99.5%) was transferred directly to the *n*-heptane with a pipette in an argon or helium atmosphere. The alkyl aluminum (Hercules Powder Co.) was also used without further purification. Solutions were prepared in a closed system and transferred to the storage bottles in an argon atmosphere. The bottles were capped with a self-sealing gasket which permitted withdrawal by a hypodermic syringe. Several solu-

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tions were analyzed to check the reliability of this method. Concentrations of the active ingredients were one molar within  $\pm 2$  per cent.

In the procedure for polymerization, petroleum ether placed in a beverage bottle was heated to vigorous boiling in a hot water bath. The amount of ether needed to allow for loss during venting was determined by two marks on the side of the bottle. After venting, during which time the contents of the bottle were stirred with a short iron rod and magnetic stirrer, solutions of the catalyst components were added, by hypodermic syringe, followed by the isoprene.

Although the sequence for introducing the catalyst ingredients was immaterial, generally, the alkyl aluminum was added first to the bottles containing the solvent and monomer. The bottles were then capped and cooled to polymerization temperature before adding titanium tetrachloride solution through the rubber-lined bottle cap.

Because the catalyst immediately flocculated and settled, the bottles were shaken vigorously. At 7° C, polymerization was so rapid that, after an hour, the increased viscosity caused the catalyst to remain suspended after shaking. Polymerization was usually completed overnight. The next morning, the polymer was soaked in methanol for 24 hours, washed on a mill during which time an antioxidant was added, and then dried overnight at 55° C in a vacuum oven.

The gel content, inherent viscosity, and infrared analyses<sup>1</sup> of the polymers were made by standard procedures.

#### DISCUSSION OF RESULTS

Early, it became apparent that the composition of the catalyst determined the amount and type of polymerization. For runs at about room temperature, the optimum ratio of alkyl aluminum to titanium tetrachloride is 1.0. If this ratio is less than 1.0, the polymer becomes less rubbery and more resinous; if the ratio is greater than 1.0, the polymers retain their rubbery characteristics but become softer and are produced in decreasing amounts. In fact, no polymer is formed if the ratio is greater than 2.0. At these high ratios, considerable isoprene is probably condensed<sup>6</sup> by the excess alkyl aluminum. A strong terpene odor was noticeable and an oily material was produced with these high-ratio catalysts, but no effort was made to identify the product.

Laboratory preparations of triethyl aluminum and triisobutyl aluminum were used initially; later, these materials were obtained from Hercules Powder Co. Practically identical polymers are produced by either the triethyl or triisobutyl compound. However, small differences between the catalysts prepared from the two compounds do exist. For example, a faster rate of polymerization is obtained by using triethyl aluminum. Likewise, there is a color differentiation at low mole ratios of alkyl aluminum to titanium tetrachloride. As the relative amount of alkyl aluminum is decreased, the color changes from dark brown to yellow, if the triethyl compound is used, and from dark brown to reddish brown in the case of the triisobutyl compound. A mud-brown color represents the correct catalyst composition with either alkyl aluminum. As the relative proportion of alkyl aluminum is increased, the catalyst becomes darker and finally black.

The data of Table I illustrate the effect of a variation in the mole ratio of alkyl aluminum to titanium tetrachloride upon the amount of gel and molecular weight, as indicated by the inherent viscosity, of the polymers. The highest

TABLE I  
EFFECT OF CATALYST MOLE RATIO ON YIELD, GEL CONTENT,  
AND VISCOSITY

Alkyl Al TiCl <sub>4</sub> , moles	Yield, %	Inherent viscosity	Gel, %
Polymerization Temp., 25° C			
0.1	30	0.10	72.0
0.2	53	0.05	51.8
0.4	50	0.11	63.3
0.6	82	0.69	44.0
Polymerization Temp., 7° C			
0.8	100	2.17	14.0
0.9	100	2.70	18.0
1.0	100	2.76	11.0
1.1	90	1.87	0.0
1.2	100	1.60	3.5
1.4	100	1.04	0.0

viscosity polymers are produced by catalysts with mole ratios of approximately 1.0. This is not extremely critical, as catalysts of mole ratio between 0.8 to 1.2 produce relatively high molecular weight polymers. Below 0.8, the amount of gel in the polymer increases rapidly, while the viscosity of the sol fraction becomes very small. Because of the high amount of gel in these samples, this viscosity becomes less indicative of the whole polymer. At these extremely low ratios, the polymers are hard infusible resins. On the other hand, if the ratio is larger than 1.2, the polymers retain their rubbery characteristics but become soft and sticky, as shown by low inherent viscosity.

The catalyst mole ratio also affects the microstructure of the polymers as shown in Table II. Polymers made from catalysts with ratios equal to or above 1.0 have a microstructure composed of about 96 per cent *cis*-1,4, 0 per cent *trans*-1,4, 0 per cent 1,2, and 4 per cent 3,4 structures, very close to that of natural rubber (98% *cis*-1,4 and 2% 3,4)<sup>1</sup>. No dependence of the microstructure upon the composition of the catalyst in this range (mole ratio  $\geq 1$ ) was observed. However, if the ratio is below 1.0, *trans*-1,4 structure appears. This is indicative of a different type of polymerization mechanism, probably cationic, caused by the excess titanium tetrachloride. The analysis of polymer produced in the low mole ratio range (0.1 to 0.6) applies to the sol fraction and represents 25 to 50 per cent of the polymer. Because of the resinous nature of

TABLE II  
EFFECT OF CATALYST MOLE RATIO ON MICROSTRUCTURE

(Et) <sub>2</sub> Al TiCl <sub>4</sub> , moles	Yield, %	% <i>cis</i> 1,4	% <i>trans</i> 1,4	% 3,4	% total found*	Comments
0.2	5	42.0	52.5	3.8	74.9	Resin
0.4	60	50.5	44.0	4.2	74.5	Resin
0.8	58	89.6	6.1	4.2	93.9	Mostly rubber
1.0	95	95.2	0.7	4.0	90.0	Rubber
1.2	100	96.1	0.0	3.9	88.0	Rubber
1.4	68	96.3	0.0	3.7	91.8	Rubber
1.6	41	95.8	0.0	4.2	85.4	Rubber
1.8	10	95.8	0.0	4.2	85.8	Rubber

\* % total found =  $\frac{100 (\text{Cis}-1,4 + \text{trans}-1,4 + 1,2 + 3,4)}{\text{Total solids}}$  (moles of C<sub>4</sub>H<sub>8</sub> units/liter).

the whole polymer, the portion insoluble in toluene would not be expected to contain less *trans*-1,4 structure.

As the amount of 3,4 structure remains constant and only a trace of 1,2 structure is ever formed over the whole range of catalyst composition, the polymerization is essentially 1,4. However, the relative amounts of *cis*-1,4 and *trans*-1,4 isomers vary, if catalysts with mole ratios less than 1.0 are used. Thus, active centers on the surface of the catalysts of different composition influence only the production of *cis*-1,4 and *trans*-1,4 isomers, in relation to each other, and not the relative amounts of 1,4 and 3,4 or 1,2 polymerization.

It was difficult to obtain optically clear solutions of some of the polymers for infrared analysis; in some instances, use of a filtering aid was necessary. The turbidity may have been caused by hydrolysis of the catalyst which, because of its fine state of subdivision, was difficult to remove. Failure to clarify the solution causes the total found to be larger than 100 per cent and fictitiously increases the amount of *trans*-1,4 structure.

Because the catalyst is an insoluble precipitate and if, as has been proposed, polymerization takes place on the surface of the catalyst particles, the amount of polymer produced in a definite time interval depends on the amount of surface available. In these experiments, it was necessary to use approximately 3.0

TABLE III  
EFFECT OF POLYMERIZATION TEMPERATURE ON  
VISCOSITY AND STRUCTURE  
(Isobutyl)<sub>2</sub>Al/TiCl<sub>4</sub> = 0.9

Polym. temp. ° C	Inherent viscosity	% gel	% <i>cis</i> -1,4	% <i>trans</i> -1,4	% 3,4	% total found
+70	0.62	0.0	94.2	1.3	4.3	89.1
+50	0.90	25.0	91.5	4.9	3.6	100.7
+25	1.35	1.5	95.8	0.0	4.1	89.7
+5	2.51	0.0	—	—	—	—

phm of total catalyst to obtain 100 per cent yield. The catalyst requirement depends upon the purity of the monomer and solvent and other experimental variables; thus, it should be possible to reduce the amount of catalyst by refinement of the experimental technique.

The molecular weight of the polymers is relatively insensitive to the catalyst level, which is indicative of the heterogeneous nature of the catalysis as contrasted to the large dependence of molecular weight on catalyst concentration that occurs in homogeneous, free radical polymerization. Catalyst concentration has no effect on the microstructure of the polymers.

Apparently, the catalyst will maintain its activity over long periods of time, if properly protected. Three bottles of identical catalyst were prepared, and after certain periods of time, isoprene was added to each bottle and polymerized. Full catalyst activity was maintained for at least 5 days.

Early polymerizations were conducted at 50° C. At this temperature, the polymerization is very fast and requires about 2 hours for completion. Lower temperatures of polymerization were tried in an attempt to raise the molecular weight of the polymer and obtain a controllable reaction. A small amount of polymer is obtained even at -78° C but the polymerization is very slow and stops at low conversion. In fact, if the temperature of polymerization is below approximately -30° C, desorption of the polymer does not appear to occur.

That is, polymer does not dissolve in the solvent but remains attached to the catalyst and deactivates it after a small amount of polymerization.

Table III contains data for a series of polymers where the effect of polymerization temperature on properties was investigated. Polymerization was conducted in 28-ounce beverage bottles that were charged from the same batch of isoprene and petroleum ether and carried to 100 per cent conversion. Decreasing the temperature decreases the velocity of the reaction, as expected, but the rate of polymerization at the three highest temperatures was so fast that the temperature surge in these three bottles must have been considerable. The inherent viscosity of the polymers is quite sensitive to the temperature of polymerization, increasing as the temperature is decreased in the normal manner.

Actual molecular size distribution in two polymers made at different temperatures was determined by fractionation of toluene solutions of the polymers. After the gel was separated, the fractions were precipitated by slowly adding methanol, isolated by decantation, and then characterized by measuring their

TABLE IV  
FRACTIONATION OF POLYMERS PREPARED AT DIFFERENT TEMPERATURES

Viscosity range	Polymerization temp.	
	15° C	-30° C
0-1	13.1	4.4
1-2	19.2	7.0
2-3	13.3	11.5
3-4	8.0	9.7
4-5	—	6.3
5-6	—	5.0
6-7	—	9.3
7-7.5	—	15.2
Microgel	36.0	23.0
Gel	0.3	1.9
Acetone extract	1.43	6.05
Whole polymer viscosity	2.0	5.2
% conversion	96	68

viscosity (Table IV). An usually high proportion of polymer precipitates within a narrow range of methanol concentration as the first fraction. This fraction has a much lower viscosity (1.0) than succeeding fractions and has the appearance of microgel. It is not known whether this was formed during polymerization or during recovery of the polymer. The low temperature polymer has a much broader distribution than the other polymer. In addition, the molecular weight distribution of the polymer made at 15° C resembles that of low temperature butadiene-styrene copolymer more than that of Hevea rubber. Thus, polymerization at -30° C results in polymer with a wider viscosity range, a higher whole polymer viscosity (5.2), and a slight decrease in the microgel.

The microstructure of the polymers, listed in Table V, indicates that a higher mole ratio of alkyl aluminum to titanium tetrachloride must be used at -30° C than at room temperature (Table II) to obtain a polymer free of *trans*-1,4 structure. Thus, catalyst with a mole ratio of 1.0, produces at -30° C polyisoprene that contains approximately 40 per cent *trans*-1,4 isomer and at room temperature essentially *trans* free polymer. If the mole ratio of the

catalyst employed at  $-30^{\circ}\text{C}$  is increased to 1.2 or 1.4, a 0 per cent *trans*-1,4 polymer is produced. The inherent viscosity data also indicate the necessity of using higher mole ratio catalysts, as the temperature of polymerization is decreased, to obtain rubbery polymers.

Although the usual concentration of monomer was a 75-25 petroleum ether-isoprene mixture, a variation in concentration was explored. Table VI lists the results for polymers prepared at concentrations of monomer from 15 to 100 per cent by volume. The rate of polymerization is quite sensitive to the con-

TABLE V  
POLYMER STRUCTURE AS A FUNCTION OF CATALYST MOLE  
RATIO AT  $-30^{\circ}\text{C}$

$(\text{Isobutyl})_2\text{Al}$ $\text{TiCl}_4$ , moles	Yield, %	Inherent viscosity	% gel	% <i>cis</i> -1,4	% <i>trans</i> -1,4	% 3,4	% total found
0.8	8	0.13	18.5	43.6	50.8	3.6	87.4
1.0	22.5	0.55	15.8	55.8	38.6	4.1	83.2
1.2	65	5.12	16.3	96.5	0.0	3.5	88.8
1.4	72	4.70	10.5	96.6	0.0	3.4	94.7

centration of monomer. Mass polymerization proceeds rapidly, and as the amount of solvent is increased, the rate becomes progressively slower. Somewhat lower molecular weight polymers are produced at high monomer concentrations.

Although petroleum ether was most extensively investigated, other solvents have been tried for the polymerization. Severe limitations are placed on choice of solvents because of the high reactivity of the alkyl aluminum and titanium tetrachloride. Another factor is the proton donor capacity of the solvent. The acidity or basicity of the catalyst is a major factor in the type of polymer

TABLE VI  
POLYMERIZATION AT DIFFERENT MONOMER CONCENTRATIONS  
(PETROLEUM ETHER)

Vol. % monomer	Alkyl Al $\text{TiCl}_4$ , moles	Polym. temp., $^{\circ}\text{C}$	Inherent viscosity	% <i>cis</i> -1,4	% <i>trans</i> -1,4	% 3,4	% total found
15	1.0	10	—	96.2	0.0	3.8	88.5
25	1.0	10	2.06	96.0	0.0	4.0	89.7
33	1.0	10	2.26	94.1	2.4	3.5	94.3
50	1.0	10	1.92	—	—	—	—
100	1.0	10	1.30	91.8	4.2	4.0	99.6
44	1.6	-30	1.55	93.7	2.6	3.6	95.1
75	1.6	-30	1.04	91.7	5.2	3.0	103.6

produced. A definitely acidic catalyst (excess  $\text{TiCl}_4$ ) will form polymer that contains considerable *trans*-1,4 structure. Consequently, the proton donor capacity of the solvent would be expected to influence the behavior of the catalyst.

Several solvents of widely different dielectric constant and sufficient chemical inertness toward the catalyst components were selected. No polymerization occurred in diethyl ether, dioxane, aniline, dimethylaniline and pyridine, but polymer was obtained in toluene, *o*-dichlorobenzene and 1-chloropentane. No polymerization occurred in basic solvents, such as aniline and pyridine, probably because of complex formation between the solvent and titanium tetrachloride. Polymer produced in toluene was very similar to that made in

petroleum ether. On the other hand, 1-chloropentane was so active that an almost explosive cationic polymerization occurred and a hard white resin was obtained.

*o*-Dichlorobenzene (dielectric constant 7.5), a slightly acidic solvent, also proved to be satisfactory for polymerization of isoprene with alkyl aluminum-titanium tetrachloride catalysts (Table VII). The velocity of polymerization is very rapid, as it required only about 1 hour at 50° C to obtain complete polymerization. Higher yields of some polymers could have been attained, but

TABLE VII  
POLYMERIZATION IN *o*-DICHLOROBENZENE

(Iso-butyl)Al TiCl <sub>4</sub> , moles	Cone. catal., phm	Polym.; temp., °C	Yield, %	% cis- 1,4	% trans- 1,4	% 1,2	% 3,4	% total found	Remarks
0.5	3.3	50	100	—	—	—	—	—	Hard white resin
1.0	0.2	25	0	—	—	—	—	—	—
1.0	0.9	25	70	86.0	9.6	0.4	4.0	93.2	Tough waxy polymer
1.5	2.9	25	100	—	—	—	—	—	Rubberly polymer
2.0	3.3	50	20	75.2	19.9	0.4	4.4	92.5	Soft sticky polymer
2.0	3.3	—10	40	91.0	4.4	0.2	4.4	84.9	Rubberly polymer
4.0	2.9	15	0	—	—	—	—	—	—

Polymerization was purposely stopped short of completion. The limited amount of data indicates that less catalyst is required for polymerization of isoprene in *o*-dichlorobenzene than in petroleum ether, and that the optimum catalyst mole ratio of alkyl aluminum to titanium tetrachloride is larger than 1.0. This would be expected in a slightly acidic solvent like *o*-dichlorobenzene. The polymer appears to be similar to that obtained in petroleum ether, although the viscosity is somewhat lower and the infrared analysis indicates the presence of a small amount of *trans*-1,4 structure.

TABLE VIII  
REPRESENTATIVE PILOT PLANT POLYMERS  
(47° to 65° F)

Alkyl Al TiCl <sub>4</sub> , moles	Cata- lyst, phm	Yield, %	Mooney M1/4- 212	Inher- ent viscos- ity	% Gel	% cis- 1,4	% trans- 1,4	% 3,4	% total found
1.2	5.34	51	17.0	2.1	1.0	95.4	0.0	4.6	86.3
1.0	2.74	62	36.0	2.4	3.0	95.6	0.0	4.4	86.8
0.8	7.67	76	34.0	1.9	25.3	96.2	0.0	3.8	91.7
0.9	8.10	96	37.0	2.0	2.8	95.9	0.6	3.4	95.4
1.0	6.41	100	43.5	2.4	22.5				
1.11	4.06	80.8	31	3.0	2.5	96.4	0.0	3.6	92.0
1.05	5.21	93.0	—	2.6	21.8	96.9	0.0	3.1	107.9

In addition to the small scale polymerization conducted in the laboratory, larger quantities of polyisoprene were prepared in a pilot plant with the alkyl aluminum-titanium tetrachloride catalysts. Usually, a 5-gallon stainless steel reactor that was equipped with a jacket and propeller type agitator was used; although, several polymers were made in a 50 gallon nickel clad reactor. The monomer concentration was reduced to 15–20 per cent by volume in petroleum ether to control the reaction and minimize the temperature surge. Thus, the finished product had enough fluidity to be drained from the polymerizer. Somewhat larger catalyst concentrations than used in the laboratory were necessary to obtain high yields in the pilot plant, undoubtedly because of less rigid

control of experimental conditions in preparing large quantities of polymers. Polymerization is essentially complete in 4 hours at 65° F, and prolonging the reaction time only increases the possibility of gel formation.

Polymerizations conducted in the pilot plant proceeded smoothly and produced polymers with structures and properties comparable to those made in the laboratory (Table VIII). The range of inherent viscosity of the polymers varies from 1.9 to 3.0, which corresponds to a spread in Mooney viscosity of 17 to 45. The microstructure of all the polymers is practically identical, amounting to 96 per cent *cis*-1,4, 0.0 *trans*-1,4 and 4 per cent 3,4 structure.

TABLE IX  
PHYSICAL PROPERTIES OF VULCANIZATES OF SYNTHETIC  
POLYISOPRENE AND HEVEA  
(Cured at 280° F)

	Gum		25 part HAF Black		50 part HAF Black	
	Hevea at 600%	Synthetic	Hevea at 300%	Synthetic	Hevea at 300%	Synthetic
<i>Modulus, psi</i>						
15 min	250	1175	825	150	1700	500
30	825	1850	1175	800	2025	1500
45	1300	2275	1200	1075	2100	2000
60	1675	2375	1250	1100	2100	2250
90	2050	2475	—	—	—	—
<i>Tensile strength, psi</i>						
15 min	1650	2425	4125	375	3700	950
30	3050	3125	4450	3700	3975	2125
45	3375	2900	4300	3650	4175	2900
60	3900	3075	4600	3100	3900	2925
90	3900	2300	—	—	—	—
<i>Elongation at break, %</i>						
15 min	980	700	650	420	550	470
30	830	680	610	620	840	410
45	760	640	600	575	540	420
60	750	640	610	570	520	410
90	700	580	—	—	—	—
<i>Forced vibrator at 100° C</i>						
Dynamic modulus, psi.	50	60	102	121	200	252
Static modulus, psi.	54	67	78	122	163	177
Internal friction, kps	0.27	0.28	1.1	1.4	3.0	5.0
<i>Firestone Flexometer</i>						
Running temp., ° F	—	—	—	—	280	310
<i>Ring tensile</i>						
At 212° F						
Tensile strength, psi	—	—	1980	1630	2385	1860
Elongation, %	—	—	560	510	530	450
At 275° F						
Tensile strength, psi	—	—	1370	1190	1615	1370
Elongation, %	—	—	560	500	535	485
<i>Ring tear, lb/in.</i>						
212° F	—	—	—	—	624	439
275° F	—	—	—	—	460	383

A limited study of the physical properties of vulcanizates of these polymers was made by the usual ASTM tests. Comparison of the properties of the synthetic polymer with those of Hevea is made in Table IX. In general, good agreement is obtained with the more extensive data of Horne and others<sup>3</sup>. Cure rate varies markedly; however, changes in catalyst, polymerization time, and gel content may account for part of this variation.

In the case of the gum vulcanizates, the most consistent results have been obtained with 1.5 phr of sulfur, 0.55 phr of benzothiazolyl disulfide, and 0.4 phr of *p*-aminophenol, which produces vulcanizates having tensile strengths of 2500

to 3200 psi. The high moduli of these cured polymers indicate crystallization at a low elongation.

Addition of 25 to 50 parts of high abrasion furnace carbon black (HAF) to the synthetic polyisoprene results in vulcanizates that compare favorably with the natural product in modulus and tensile strength, at both room and elevated temperatures. However, the internal friction of vulcanizates containing carbon black is higher than that for the corresponding natural rubber vulcanizates. This is consistent with, and is the cause of the higher running temperature of the 50-part HAF vulcanizate. It may result from the generally low molecular weight of the synthetic polymers that were investigated.

#### CONCLUSIONS

By adjustment of the relative amounts of the two components of the catalyst and the temperature of polymerization, *cis*-1,4 polyisoprene can be produced free from *trans*-1,4 configuration. Catalysts containing a mole ratio of alkyl aluminum to titanium tetrachloride of 1.0 produce polymers with this configuration at room temperature. At lower temperature of polymerization, somewhat higher ratios are needed to achieve the same result.

Solution polymerization was used to control the reaction and obtain a uniform product. It was necessary to use 3 to 5 phm of total catalyst to obtain 100 per cent yield in 4 hours at room temperature. The inherent viscosity of the polymers made under these conditions is low, usually 2.0 to 2.5. However, higher molecular weight polymers are produced at lower polymerization temperature.

Compounding studies indicate that vulcanizates of these polymers possess both normal and hot tensile properties comparable to natural rubber. Hysteric properties of the carbon black vulcanizates of the polymers studied are inferior to those of natural rubber.

#### ACKNOWLEDGMENT

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## PERDEUTERIO SN RUBBER \*

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The recently reported stereospecific polymerization<sup>1</sup> of isoprene and the availability of D<sub>2</sub>O has made possible the preparation of synthetic-natural (SN) rubber in which most of the hydrogen atoms are D atoms.

Acetone-d<sub>6</sub> was prepared<sup>2</sup> from 99.5 per cent D<sub>2</sub>O and acetone-h<sub>6</sub> in the presence of K<sub>2</sub>CO<sub>3</sub>. Nine stages were applied. Each required fractionation of acetone from water, and it is estimated that each replaced approximately half of the light hydrogen remaining from the previous stage. Acetylene-d<sub>2</sub> was prepared from D<sub>2</sub>O and calcium carbide. The procedure of Bergmann<sup>3</sup> for the Favorski<sup>4</sup> reaction of acetylene and acetone to form 2-methyl-3-butyn-2-ol was followed except that in our work perdeuterio reactants were used.

The triple bond of the butynol selectively absorbed D<sub>2</sub> over the Lindlar<sup>5</sup> catalyst, and the resulting 2-methyl-3-butene-2-ol dehydrated readily over Al<sub>2</sub>O<sub>3</sub> to give isoprene-d<sub>8</sub>. Standard fractionation techniques were used for the isoprene and for all the intermediates. The isoprene was finally distilled over sodium to remove acetylenes, acetone, and alcohols. The same methods were applied to the corresponding perprotio derivatives. Table I gives the properties of most of the compounds prepared and used in this study.

The isoprene-d<sub>8</sub> polymerization was initiated by TiCl<sub>4</sub> and triisobutyl-h<sub>27</sub>-aluminum in both aliphatic and aromatic solvents. Hydrogen from these solvents did not appear to interchange with deuterium from the monomer or polymer. Isoprene-d<sub>8</sub> polymerizes faster and to a higher molecular weight than isoprene-h<sub>8</sub> under what are believed to be comparable conditions. Our best sample of D-SN rubber was prepared by hexane extraction of a raw polymer containing 25 per cent gel. The soluble polymer ( $M_n = 333,000$ ) milled (broke down) like natural rubber and had a limiting intrinsic viscosity in benzene at 25° of  $[\eta]_0 = 5.8$ .

The benzene solutions were found to degrade unless they were stabilized with a small amount of tetramethylthiuram disulfide (TMTD). D rubber evolved<sup>6</sup> a trace of D<sub>2</sub> when it was vulcanized with TMTD and ZnO. The vulcanizate, after removal of zinc compounds and other substances by short-path distillation techniques<sup>7</sup>, was nearly transparent and displayed an x-ray diffraction pattern that was superposable over those of natural and SN rubbers. The density at 23° C of the vulcanizate was 1.010 g/ml (equivalent to 1.009 at 25° C); and the density of the polymer before cure was 1005 g/ml (equivalent to 1.003 at 25° C). Accepting 0.906 g/ml at 25° C as the density of purified natural rubber<sup>8</sup> and multiplying this by the ratio (1.118) of the density of isoprene-d<sub>8</sub> to the density of isoprene-h<sub>8</sub> (see Table I), we obtain a calculated value of 1.013 g/ml for the density of D rubber. Now the ratio of the formula weight (76.145) of isoprene-d<sub>8</sub> to that (68.119) of isoprene-h<sub>8</sub> is

\* Reprinted from *Science*, Vol. 128, p. 359 (1958).

1.118. It is probable that 0.906 is somewhat high as the density of perproto all-*cis*, 1,4-head-to-tail polyisoprene, and values observed for some of our best samples of SN rubber are around 0.901. This, when multiplied by 1.118, gives 1.007 as the expected density of D-SN rubber. The good agreement between the found and expected values of the density shows that our specimen contains at most not more than a few hydrogen atoms.

Study of the boiling points given in Table I reveals, except for water where hydrogen-bonding is important, that the perdeuterio derivatives boil at lower temperatures than the corresponding perproto compounds. Assuming boiling point to be a measure of molecular interaction in small molecules and to be of value for predicting segment interaction in a related polymer, it is expected that there would be less polymer-polymer interaction in the case of D rubber than

TABLE I  
PROPERTIES OF PERPROTO AND PERDEUTERIO DERIVATIVES  
OF COMPOUNDS AND AZEOTROPIC MIXTURES

Compound or azeotrope	Boiling point (740 mm)	Freezing point	Water (wt. %)	$n_{D}^{20}$	$d_4^{20}$
Perproto derivatives of compounds and mixtures					
Acetone	55.3			1.3592	0.7895
Water	99.2	0.0	100	1.3333	0.99823
2-Methyl-3-butyn-2-ol	103	3.0		1.4215	0.8609
2-Methyl-3-butyn-2-ol water azeotrope	89.0	-10.5	27	1.4050	
2-Methyl-3-buten-2-ol	96.5	-28.0		1.4172	0.8231
2-Methyl-3-buten-2-ol water azeotrope	85.3	-9.0	23.2	1.4078	
Isoprene	33.3			1.4219	0.6802
Perdeuterio derivatives of compounds and mixtures					
Acetone	54.3			1.3565	0.8719
Water	100.6	3.8	100	1.3286	1.1075
2-Methyl-3-butyn-2-ol	102	1.9		1.4188	0.9423
2-Methyl-3-butyn-2-ol water azeotrope	89.5		27	1.4034	
2-Methyl-3-buten-2-ol	96.0	-28.8		1.4134	0.9185
2-Methyl-3-buten-2-ol water azeotrope	86.0		20.0	1.4053	
Isoprene	31.8			1.4189	0.7604

in the case of H rubber. This expectation is confirmed by the interaction coefficient,  $\mu_1$ , found by study of toluene solutions which revealed a value of 0.415 compared with 0.398 for H-SN rubber. It is tempting to predict, therefore, that the dynamic properties of D rubber will be found to be better than those of H rubber.

The infrared spectrum of D-SN rubber is of special interest. For example, it contains a band at  $15.20 \mu$  corresponding to the  $11.95 \mu$  band in H rubber. This finding confirms the previously somewhat doubtful assignment of the  $11.95 \mu$  wavelength to the H atom on the double bond.

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# THE MECHANISM OF PROTECTION BY THE DEACTIVATING EFFECT \*

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## INTRODUCTION

It is known that some substances, called deactivators, an example of which is the zinc salt of mercaptobenzimidazole, protect vulcanized rubber against aging by a mechanism differing from that of conventional antioxidants<sup>1,2</sup>. Antioxidants reduce to a greater or lesser extent the rate of oxygen absorption by the autoxidizable substance; on the other hand, deactivators markedly delay the deterioration in mechanical properties during aging, although absorption is not affected appreciably. The theory previously advanced to explain their action was that a deactivation of primary peroxides occurred, producing the fixation of oxygen upon the molecular chain without involving any scission. It was suggested that the combined action of a deactivator and an antioxidant could improve protection against aging, and this was actually confirmed by experimental results<sup>3</sup>. For a general survey of rubber protection by means of the deactivating effect see Reference 13.

This theory did not, however, seem to be entirely satisfactory. Le Bras and Salvetti had noted that deactivators are not only unable to protect raw rubber against degradation by oxygen<sup>4</sup>, but even cause a rapid lowering of the viscosity of solutions<sup>5</sup>. Such observations were confirmed by Kendall<sup>6</sup> who reported that mercaptobenzimidazole reacts with hydroperoxides to form radicals, and considerably accelerates the aging action of peroxides on rubber solutions or latex.

On the other hand, research aimed at relating the deactivating effect to chemical structure<sup>7,8</sup> showed the presence of a thiol group to be necessary, the carbon atom carrying this group being located by preference either between two nitrogen atoms or one nitrogen and one oxygen atom and a cyclic structure being a favorable factor. This is the case, for instance, for mercaptobenzimidazole, mercaptopyrimidine, and mercaptobenzoxazole. These compounds are closely related to certain vulcanization accelerators, in particular the mercaptobenzothiazole types, and it is therefore not surprising that a marked effect of mercaptobenzimidazole (MBI) on vulcanization has been noted<sup>7,9,10</sup>. It was for this reason that the use of the zinc salt as a deactivator for this compound (MTBZ), whose effect on vulcanization is much smaller<sup>7</sup>, was recommended. Even with MTBZ the effect on vulcanization is far from negligible, especially when the accelerator is a basic product, such as diphenylguanidine. Accordingly we have observed in this case that MTBZ reduces the optimum curing time from 60 to 45 minutes, with an associated improvement in mechanical properties. Conversely, with an acid accelerator, such as mercaptobenzothiazole, a slight delay in curing is noted when using MTBZ.

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In view of the effect on vulcanization, Shelton and Cox<sup>11</sup> thought that the action of deactivators could be explained by their interaction with the primary vulcanizate structure. Similarly, Haehl<sup>12</sup> wrote about the formation of a "stabilized" structure of vulcanizate.

The variation in the protective action of the MTBZ with the nature of the accelerator and the increase in effectiveness when the compound is undercured, which will be shown later, must also be taken into account.

It is difficult to explain all these facts by the action of MTBZ solely upon either oxygen or peroxides, and therefore Le Bras and Le Foll<sup>8</sup> suggested that deactivators favor a delayed formation of intermolecular links. This idea was later expanded by saying that "to all appearances, the deactivator is able to repair, when they occur, the damages caused by oxidation of the vulcanizate structure, i.e., create new crosslinks as substitutes for the scissions caused by oxygen<sup>13</sup>".

However, as the experimental data were insufficient to support this theory, it has been necessary to extend the preliminary experiments<sup>9</sup>. In this way, we have been able to gather a set of results to support this mechanism<sup>14</sup>. We shall give here a detailed account of these experiments, together with some new data.

#### RELAXATION MEASUREMENTS AND MECHANISM OF THE DEACTIVATING EFFECT

In order to determine the specific action of deactivators, we have used the physical relaxation measurement method as evolved by Tobolsky<sup>15</sup>. The deactivator used in all our experiments was the zinc salt of mercaptobenzimidazole (MBTZ).

#### THE PRINCIPLE OF THE METHOD

In a sample held at constant elongation, the stress decreases with time at a rate varying with both the type of the compound and the testing temperature. After a sufficiently long time, the stress may even be reduced to zero.

The resulting stress-time curve is approximately a decreasing exponential corresponding to the equation:

$$\sigma = \sigma_0 e^{-Kt}$$

where  $\sigma$  is the stress at time  $t$ ,  $\sigma_0$  the initial stress, and  $K$  a rate constant which depends upon the absolute temperature and the free energy of activation of scission. This activation energy is related here to the energy required for the oxidative rupture of chemical links. It is clear that the lower this energy, the higher will be the rate of stress relaxation at a given temperature. It is to be expected that a vulcanizate will be more easily degraded by heat or oxidation when the chemical links in its network are more oxidizable. As a result, the extent of relaxation of a given vulcanizate may give indications as to its behavior during normal aging, the more so since such relaxation measurements are made at temperatures over 70° C, i.e., in the range where scission of chemical bonds predominate.

When "continuous" relaxation is measured, i.e., when the testpiece is maintained at the same elongation all the time, the final value of the stress is not affected by crosslinks which are formed during aging and which increase, as is known, the tensile strength<sup>16</sup>. It is considered that such links are formed on already strained chains and do not, consequently, contribute to the stress.

Therefore, the extent of relaxation depends exclusively, in this case, on the number of molecular scissions produced in the sample during a given time.

It is also possible to study "intermittent" relaxation by stretching the sample periodically (every 2-3 hours for instance) to a given elongation and releasing it after measuring the stress. In this case, the crosslinks which may be formed in the sample at rest will play a part when the stress is determined, so that lower stress decays will be observed than with continuous relaxation procedure for the same vulcanizate. It is clear that a true comparison is only possible when the two sets of measurements are carried out under rigorously identical conditions of temperature and elongation.

The creation of crosslinks during aging is thus indicated by the difference between "continuous" and "intermittent" relaxation values.

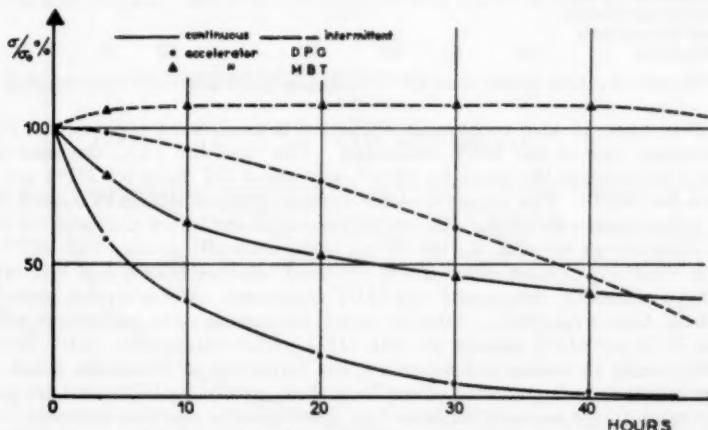


FIG. 1.—Continuous and intermittent relaxations of pure-gum vulcanizates accelerated with diphenylguanidine and mercaptobenzothiazole.

#### EXPERIMENTAL RESULTS

The experiments were made at a temperature of 100° C and an elongation of 50%, i.e., inside the range of validity of the above-mentioned equation, according to the thermodynamic theory of elasticity. The experiments were carried out with a relaxometer allowing easy measurement of both types of relaxation<sup>17</sup>.

*Respective effects of one antioxidant and one deactivator.*—The curves in Figure 1 give, on the basis of the values in Table I, the continuous and intermittent relaxations for two pure-gum type vulcanizates differing in the nature of the accelerator, diphenylguanidine (DPG), and mercaptobenzothiazole (MBT).

#### Recipe:

Rubber	100
Stearic acid	1
Zinc oxide	3
Sulfur	3
Accelerator	1

Optimum cure at 143° C was 60 minutes with DPG and 25 minutes with MBT.

TABLE I

Heating time, hrs.....	10		20		30		40	
Compound .....	DPG*	MBT*	DPG*	MBT*	DPG	MBT	DPG	MBT
<b>Continuous relaxation</b>								
$\sigma, \lambda \text{ kg/cm}^2$	2.4	3.4	1.05	2.8	0.39	2.4	0.06	1.9
$\sigma/\sigma_0, \%$	37	65	16	53	6	45	1	36
<b>Intermittent relaxation</b>								
$\sigma, \text{kg/cm}^2$	6.1	5.7	5.3	5.7	4.1	5.7	3.04	5.7
$\sigma/\sigma_0, \%$	92	108	80	108	62	108	46	108
Difference in % between continuous and intermittent relaxation	55	43	64	55	56	63	45	72

\* The value of  $\sigma_0$  is  $6.6 \text{ kg/cm}^2$  for the DPG compound and  $5.3 \text{ kg/cm}^2$  for the MBT compound.

It is observed that continuous relaxation is much more rapid in the DPG compound than in the MBT compound. The "half-life", i.e., the time necessary to decrease the stress by 50%<sup>18</sup>, was about 5.5 hours for DPG and 24 hours for MBT. This means that the various types of crosslinks formed during vulcanization under the influence of these accelerators are not endowed with the same energy of scission, this energy being markedly greater with MBT.

A relatively greater difference is observed between continuous and intermittent relaxation values with the MBT compound, after a certain period of heating, than with DPG. After 40 hours, for instance, the percentage difference is 72 for MBT against 45 with DPG. This means that MBT favors, during aging as during vulcanization, the formation of crosslinks which are more resistant to degradation effects than those created by DPG, and are probably more numerous, as is confirmed by the respective modulus increases. On the other hand, it is evident that an antioxidant intended to prevent oxygen from breaking crosslinks should produce a reduced number of scissions during

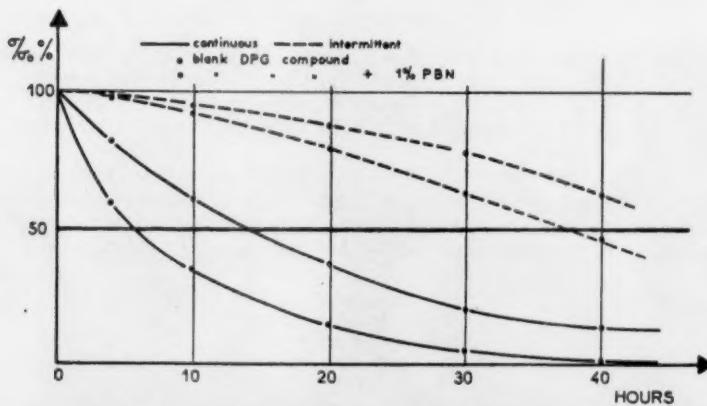


FIG. 2.—Effect of an antioxidant (phenyl-2-naphthylamine) on the relaxation of a diphenylguanidine vulcanizate.

a given time and, consequently, reduced relaxation. This is clearly shown by the curves of Figure 2: the introduction of phenyl-2-naphthylamine in a compound accelerated with DPG increases the half-life from 5.5 hours to 14 hours, but the differences between continuous and intermittent relaxation do not vary much, which means that the main effect of the antioxidant is limited to reduction of the scission reaction. The same phenomena are noted with a vulcanizate accelerated with MBT and protected with phenyl-2-naphthylamine (see Curves T and T + A in Figure 4).

If we consider now a product inert towards oxygen but which is able to create crosslinks during aging, we may forecast no changes during continuous relaxation, and a marked increase in the values of intermittently measured stress, i.e., a smaller amount of intermittent relaxation. This is exactly what is observed with MTBZ. According to the curves in Figure 3, the half-life is prac-

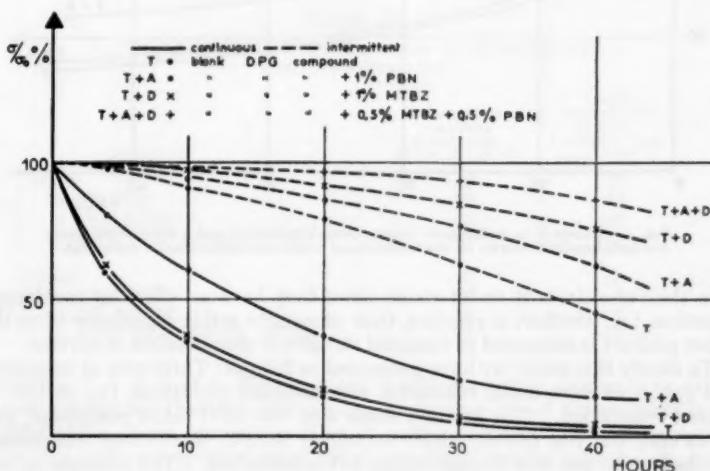


FIG. 3.—Effects of an antioxidant (phenyl-2-naphthylamine) and a deactivator (sine mercaptobenzimidazolate) on the relaxation of a diphenylguanidine vulcanizate.

tically unchanged in the vulcanizate containing the deactivator. Conversely, the difference after 40 hours between the two types of relaxation is increased from 45 per cent (for the blank) to 75 per cent, which can be explained only by additional crosslinking, since scissions are not inhibited by MTBZ.

On the basis of these observations, we conclude that MTBZ protects the vulcanizate not by acting as a barrier against oxygen but by acting as a crosslinking agent.

In the case of an MBT vulcanizate, the difference between continuous and intermittent relaxation to the blank is changed less by MTBZ than with a DPG compound, as is shown in Figure 4. However, we have seen from Figure 1 that MBT induces much crosslinking during aging, so that we may suggest that MTBZ, in the presence of a substance which can produce similar effects, cannot make any important contribution of its own to this creation of crosslinks.

*Consequences related to aging.*—The mechanism of the action of deactivators thus determined, the next question is whether or not their behavior is modified

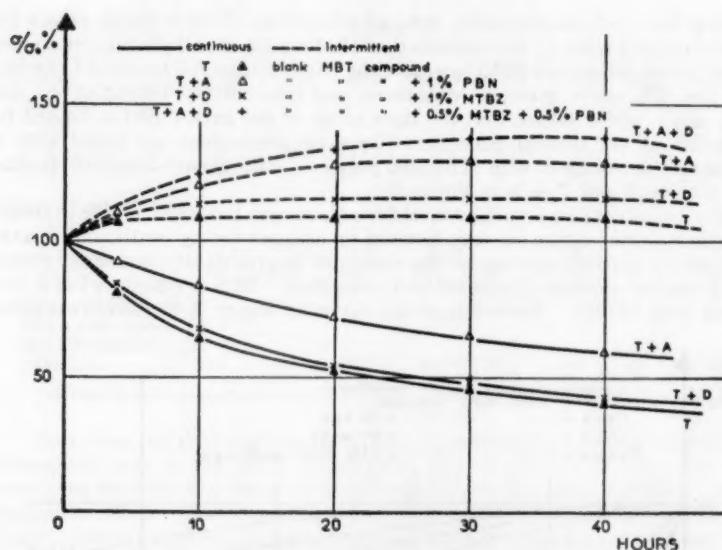


FIG. 4.—Effects of an antioxidant (phenyl-2-naphthylamine) and a deactivator (since mercaptobenzimidazolate) on the relaxation of a mercaptobenzothiazole vulcanizate.

when the vulcanizate is under stress, since they have no effect on continuous relaxation, i.e., whether, in practice, their protective action disappears when the rubber product is subjected to repeated stresses or compressions in service.

To clarify this point, we have proceeded as follows: Three sets of testpieces were put in an oven under relaxation measurement conditions, i.e., at 100° C without ventilation. The first set, made with the DPG blank compound, was left at rest, the two others, which contained MTBZ, were either maintained stretched at 50 per cent elongation, or left unstretched. The decrease in mechanical properties after 24 hours of aging (Table II) shows that protection by MTBZ is unchanged, within experimental error, whether the compound be stretched or not.

Consequently, the behavior of MTBZ is not modified when the vulcanizate is stretched.

A second question is whether or not the formation of crosslinks by the deactivator as shown by tests at 100° C occurs also at normal temperatures. In other words, is there a temperature limit below which MTBZ is ineffective, i.e., is the protection shown by accelerated aging tests also applicable to natural aging?

TABLE II

Compound	Initial tensile strength, kg/cm <sup>2</sup>	Tensile strength after 24 hrs at 100° C, kg/cm <sup>2</sup>	Loss %
DPG blank (at rest)	270	100	60
DPG + MTBZ (opt.) (at rest)	285	170	40
DPG + MTBZ (opt.) (stretched at 50%)	285	165	43

In order to investigate this point, two vulcanizates were prepared, one with DPG, one with MBT, with or without MTBZ, and left for shelf aging at room temperature.

The first determinations of tensile strength after 6 months of such natural aging showed a notable protection by MTBZ in the case of the DPG compound, but no differences, yet, for the MBT compound. Such tests should, of course, be continued much longer so that the differences between the various compounds might be clearly assessed. However, from the result noted with DPG, it is already clear that the deactivator is also active at room temperature.

*Combined effects of an antioxidant and a deactivator.*—It was also interesting to see if relaxation measurements could account for the synergistic effects observed in aging tests when an antioxidant and a deactivator are simultaneously added to a compound, often described in literature<sup>8,7,8,11,12,19,20,21</sup>.

TABLE III  
COMBINED EFFECTS ON AGING OF AN ANTIOXIDANT  
AND A DEACTIVATOR

Compound	Intermittent relaxation $\sigma/\sigma_0\%$ after 40 hrs at 100° C	Tensile strength loss % after 3 weeks in Geer oven at 80° C
DPG {	Blank	46
	+ 1% PBN	52
	+ 1% MTBZ	75
	+ 0.5% PBN + 0.5% MTBZ	86
MBT {	Blank	-8
	+ 1% PBN	-28
	+ 1% MTBZ	-16
	+ 0.5% PBN + 0.5% MTBZ	-37

Curves *T* + *A* + *D* in Figures 3 and 4 indicate better resistance to intermittent relaxations than for vulcanizates containing one of these agents only, an illustration of the synergistic effect of such a combination. These results are in line with conventional accelerated aging test results indicated together with the intermittent relaxation values in Table III.

#### FURTHER CONFIRMATIONS OF THE SUGGESTED MECHANISM

On the basis of the experiments described above, protection by deactivators is explained by the creation, during aging, of additional crosslinks which, added to those which the accelerator can create by itself, reinforce the structure of the vulcanizate, repair the damage brought about in it by oxidative scission, and thereby maintain the mechanical properties. To obtain a clearer idea of the way in which this theory has evolved, several considerations should be taken into account:

- (1) A given accelerator will create, during vulcanization, some crosslinks, the number, nature, and distribution of which are specific for this accelerator and govern the mechanical properties of the vulcanizate.
- (2) Such crosslinks resist oxidative degradation differently, as illustrated by the continuous relaxation curves.
- (3) The same holds for crosslinks produced during aging; for these, two factors are important, their relative resistance and their number.

TABLE IV  
FREE SULFUR IN UNAGED VULCANIZATES FOR  
DIFFERENT CURING TIMES

Curing time at 143° C., min	Reference DPG			DPG + 1% MTBZ		
	Tensile strength, kg/cm <sup>2</sup>	Free S	Total S %	Tensile strength, kg/cm <sup>2</sup>	Free S	Total S %
10	140	1.45	48	160	1.1	36
20	185	1.22	40	210	0.90	30
30	210	0.95	31	250	0.60	20
45	250	0.64	21	280	0.30	10
60	260	0.35	11	260	0.20	6

(4) Scissions created in the network by degradation may involve either the parts of rubber hydrocarbon chains located between two crosslinks, or these bridges, or the junction points of the crosslinks and chains, although the conclusions of the authors who have tried to clear up this point<sup>22-26</sup> differ somewhat.

(5) Finally, it is evident that the deactivator does not necessarily create a new link at the point where a scission occurred. We should consider statistically the whole set of scissions and new crosslinks which maintain an adequate degree of crosslinking in the vulcanizate.

To learn something more about this mechanism, it was useful to have some indications of the nature of links the deactivator could create. Since the deactivator's action on crosslinking is similar to the action of accelerators, the immediate assumption was that it worked in the same way, i.e., by mobilizing sulfur for creating intramolecular links. It seemed therefore possible to draw useful indications from a measurement of the free sulfur content of vulcanizates.

#### INFLUENCE OF THE DEACTIVATOR ON THE FREE SULFUR RATIO

Free sulfur was measured by the conventional hyposulfite method<sup>27</sup>. Combined sulfur is estimated by difference with total introduced sulfur (3% in all cases).

*Case of DPG vulcanizates.*—We first determined the free sulfur in unaged samples, DPG accelerated, vulcanized for different times, and with and without MTBZ (Table IV). The same determination was made with optimum cured compounds, after varying aging periods in an oven at 80° C (Table V).

Table IV shows that the amount of free sulfur is consistently lower when MTBZ is present. This agrees with the experimental observation that the vulcanization reaction of compounds accelerated with DPG is activated by

TABLE V  
COMBINATION OF FREE SULFUR DURING AGING

Aging at 80° C., days	DPG (optimum 60 min)		DPG + MTBZ (optimum 45 min)	
	Free S		Free S	
	Parts	% comb. by aging	Parts	% comb. by aging
0	0.35	0	0.30	0
5	0.24	31	0.15	50
10	0.17	51	0.10	67
15	0.16	54	0.06	80

MTBZ. We have also seen (Figure 3) that both the blank vulcanizate and the one with MTBZ, when compared at their respective optimum cures, give practically identical continuous relaxation curves, which indicates similar networks. It is therefore likely that, in the presence of DPG, the part played by MTBZ in vulcanization is limited to activating the main accelerator. This results in a more rapid consumption of free sulfur (and a higher number of crosslinks created in a given time), but without modifying the nature of the links which remain characteristic of the DPG.

As regards measurements made during aging, it appears that initial free sulfur is also more rapidly combined when MTBZ is present than in the blanks (Table V). The additional crosslinking shown by the intermittent relaxation curves in Figure 3 may thus be explained, in part at least, by sulfur-type cross-links formed under the influence of MTBZ.

TABLE VI  
CONSUMPTION OF FREE SULFUR IN MBT VULCANIZATES

Vulcanization time at 143° C., min.	MBT blank			MBT+1% MTBZ		
	Tensile strength, kg/cm <sup>2</sup>	Free S, %	Total S %	Tensile strength, kg/cm <sup>2</sup>	Free S, %	Total S %
5	120	1.34	44	110	1.42	47
10	105	0.98	32	145	1.04	34
15	215	0.68	22	170	0.71	24
20	220	0.49	16	190	0.53	18
30	210	0.26	8	205	0.51	17

Aging at 80° C., days	MBT blank (optimum 25 min)			MBT+1% MTBZ (optimum 30 min)		
	Free S, %	Init. free S comb. Init. free S	×100	Free S, %	Init. free S comb. Init. free S	×100
0	0.49	0		0.51	0	
5	0.27	44		0.27	52	
10	0.17	65		0.16	72	
15	0.11	78		0.08	84	

*Case of MBT vulcanizates.*—When free sulfur is determined, as in the previous case, in MBT vulcanizates, first for vulcanization times and then for different aging times, the results, as indicated in Table VI, show that: (a) during vulcanization, sulfur combines somewhat more slowly in the presence of MTBZ; (b) during aging, MBT has an important after-cure effect, the combination of free sulfur being much more important than with DPG; and (c) only a slight increase of the rate of consumption of sulfur is then produced by MTBZ as compared to the blank, i.e., a much less important increase than with DPG vulcanizates.

Consequently, although the rate of vulcanization is decreased by MTBZ, this compound plays a distinctive part in the formation of sulfur-type crosslinks during aging. However, as MBT is a much more potent aftercure agent than DPG, it is clear that, owing to the competition between MBT and MTBZ for the combination of free sulfur, the efficiency of MTBZ is relatively lower and the additional protection less important.

*Consequences.*—Since MTBZ, as all accelerators, can bring about the formation of sulfur-type crosslinks, it was thought useful to check its effect as sole accelerator on the vulcanization of a pure-gum compound. On heating to 143° C a compound containing 3 parts sulfur and 1 part MTBZ for 100 parts rubber,

TABLE VII  
INFLUENCE OF DEGREE OF VULCANIZATION ON DPG VULCANIZATES

Aging at 80° C., days	Consumption of free S Init. free S comb. $\times 100$		Tensile strength variations, loss %			
	DPG under- cured	DPG + MTBZ under- cured	Optimum		Underscured	
			DPG	DPG + MTBZ	DPG	DPG + MTBZ
5	11	22	36	27	54	18
10	21	36	95	70	100	49
15	25	48	—	96	—	73

it was observed that the compound had set-up after about 30 minutes. Optimum cure is around 2.5 hours and tensile strength 130 kg/cm<sup>2</sup> (1850 lb/sq in). MTBZ is therefore an extremely slow accelerator of the acid type.

By adding 1 per cent dibutylamine to the compound, the activating action of this base on acid acceleration is particularly apparent since optimum cure is reduced to 20 minutes while tensile strength is increased to 280 kg/cm<sup>2</sup> (3980 lb/sq in).

On the other hand, it is possible that the presence of free sulfur is necessary to allow MTBZ to exert its protective effect on the vulcanizate, this effect being absent when vulcanizing agents other than sulfur (or related products) are used. As a matter of fact, no improvement in aging is given to dicumyl peroxide vulcanizates by MTBZ.

#### NATURE OF THE CROSSLINKS PRODUCED BY THE DEACTIVATOR

The above experiments are consistent in showing that the deactivator acts during aging to create sulfur-type crosslinks. It seemed useful to have also

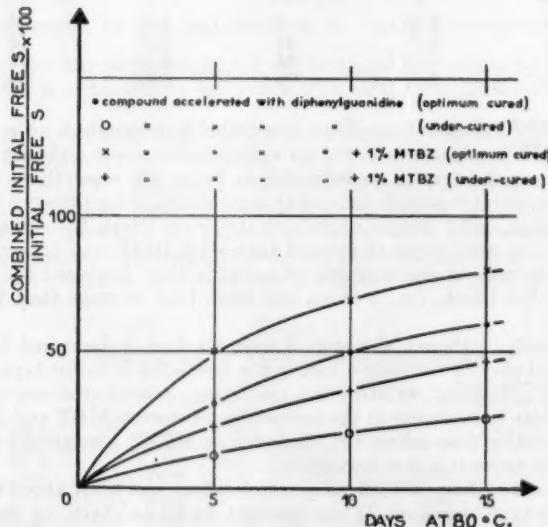


Fig. 5.—Influence of zinc mercaptobenzimidazolate on the combination of free sulfur during aging, in the case of an optimum-cured or an under-cured diphenylguanidine compound.

some indications on the characters of such links, as compared to those simultaneously produced by the accelerator.

In the case of DPG acceleration, we saw that from the shape of continuous relaxation curves (Figure 3) MTBZ appeared to be acting as an activator only, without markedly affecting the nature of links created by the accelerator since the half-life stays around 5.5 hours. It seems that the case is different during aging, as indicated by a comparison of aging tests at 80° C on optimum-cured and under-cured compounds.

In Table VII variations in free sulfur contents are given for under-cured compounds (20 min at 143° C), together with tensile strengths for both these and optimum-cured compounds. The curves of Figures 5 and 6 are plotted from these results, supplemented by data from Table V.

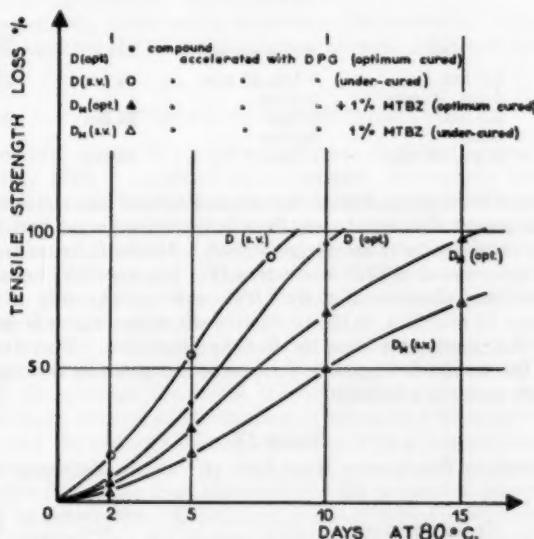


FIG. 6.—Influence of zinc mercaptobenzimidazolate on the variation of tensile strength during aging, in the case of an optimum-cured or an under-cured diphenylguanidine compound.

It will be noted first that for optimum-cured compounds, MTBZ exerts an efficient protection against degradation. This effect, however, can be related to the resultant increase in combined sulfur without any indication as to the nature of corresponding additional crosslinks. If we consider now the case of under-cured compounds, we see that for a given period of aging the blank is more quickly degraded when curing time is reduced, while the contrary is true in the presence of MTBZ. It is also observed that a relatively greater proportion of free sulfur is mobilized under the influence of MTBZ in under-cured compounds.

Therefore notable differences are manifest in the behavior of MTBZ during curing and aging, probably because of the influence of temperature on the respective rates of reaction of DPG and MTBZ. We may infer that during the more moderate after-cure conditions which occur during aging, MTBZ is able

to play a greater part than during vulcanization proper and to bring about the formation of a characteristic type of crosslink which is more resistant to degradation. Since the chemical constitution of MTBZ is akin to mercaptobenzothiazole, such links could be similar to those created by this accelerator. In any case, if there is a variation in the nature of the links, this should be reflected in the half-life values of variously aged samples. This is confirmed by the results given in Table VIII.

It is seen that the half-life of the blank is slightly improved by aging; this would normally be explained by changes in the initial structure of the network which occur during heating in air<sup>16,23</sup>. If such changes create crosslinks rela-

TABLE VIII  
VARIATION OF HALF-LIFE, IN HOURS, DURING AGING

Aging at 80° C., days	DPG	DPG + MTBZ	MBT	MBT + MTBZ
0	5.5 hrs	5 hrs, 40 min	24 hrs	24 hrs
5	5 hrs, 10 min	5.5 hrs		
10	5.5 hrs	6 hrs	24 hrs	24 hrs
15	6 hrs	6.5 hrs		
20	6 hrs, 10 min	7 hrs	24 hrs	24 hrs

tively more resistant to degradation, we can understand why continuous relaxation, which measures this resistance, then indicates a longer half-life, despite the lower conventional mechanical properties. As the increase in half-life is greater in the presence of MTBZ, we deduce that the crosslinks formed by it are more resistant than those created by DPG, and consequently of a different nature. It may be said that, in the protective effect, free sulfur is more usefully mobilized by the deactivator than by diphenylguanidine. Therefore, as demonstrated by the results in Figure 6, the protection given by it is more efficient when more free sulfur is available.

TABLE IX  
CONTINUOUS RELAXATION HALF-LIFE OF VARIOUS VULCANIZATES

Type of vulcanizate	Optimum vulcanization time	Half-life	
Rubber 100, sulfur 7 p	4 hrs	3 hrs	
Rubber 100 p Sulfur 3 p Zinc oxide 3 p Stearic acid 1 p	MTBZ Mercaptobenzimidazole MTBZ + dibutylamine (1 p) DPG MBT	2.5 hrs 1.25 hrs 20 min 60 min 25 min	5.5 hrs 9 hrs 18 hrs 5.5 hrs 24 hrs

In the case of *MBT acceleration*, however, similar experiments with vulcanizates, aged for different times, show that practically no alteration in half-life is caused by MTBZ. The inference is that the links created under the influence of MTBZ are similar to those produced by MBT, which is likely enough since the two products belong to similar chemical families. In this case, therefore, the character of the network is not profoundly modified by MTBZ, and it is to be expected that the resultant protection is relatively weak and arises simply from some additional crosslinking.

In order to have some idea of the relative resistance of the links and thus

confirm the view expressed above, it was necessary to determine the half-life of vulcanizates cured by using the deactivator as accelerator. These values are given in Table IX, together with the figures for other types of compounds.

It appears that when the curing time is decreased by using mercaptobenzimidazole, which is more active than the zinc salt, or by activating the latter by dibutylamine, the half-life is increased and can attain a value of 18 hours not far from the 24 hours of the MBT vulcanizates. For long vulcanization times, it is evident that besides the crosslinks created under the influence of the accelerator, a substantial proportion of links is certainly created through the action of sulfur only, and such links are, as we know<sup>13</sup>, of the polysulfide type and not very resistant to aging. As the half-life is based upon all these crosslinks, it is understandable that its variation is more sensitive to the accelerator used when the vulcanization time is shorter.

It seems possible, therefore, to infer from the results in Table IX that the crosslinks created by MTBZ are stronger than with DPG and about as strong as with MBT.

#### THEORETICAL CONSIDERATIONS

*The deactivator effect.*—From the experiments described, we may deduce that the deactivating effect is explained by a formation of crosslinks which repair the damage caused by scissions in the three-dimensional network of the vulcanizate. A deactivator may be regarded as a very slow-acting accelerator which, by favoring combination of free sulfur during aging, causes the formation of specific intermolecular chemical links. The resultant protection will therefore be more efficient when these links are more resistant to degradation than those links produced by the accelerator used.

Therefore, when comparing antioxidants and deactivators, it may be said that with an ideal antioxidant, no network changes take place and with an ideal deactivator, the average density of the network chains is unchanged during aging. However, instead of eliminating scissions as first suggested, deactivators make good the scissions by new crosslinks with a concomitant retention of mechanical properties.

In practice there is no ideal behavior and the protective power of either the antioxidant or deactivator will be more or less manifest according to the structure of the network, i.e., the nature of the vulcanizing system we use. Aging conditions also play a part, since degradation is caused by both oxygen and heat. It may be thought that this thermo-oxidative action can, according to the temperature and other factors, affect certain parts of the network preferentially, i.e., either portions of the macromolecular chain, or crosslinks, or crosslinks connections. Different energies are needed for the rupture of these links according to their nature. (On this point, fundamental research carried out by BRPRA<sup>29</sup> on the oxidation of organic sulfides may afford valuable information on the resistance to oxidative degradation of the different types of crosslinks.)

Furthermore, from the numerous observations made by comparing oxidizability and aging in the presence either of antioxidants or deactivators, it may be concluded, as we have already mentioned<sup>1</sup>, that each type of these protective agents is endowed with both mechanisms of action, with a more or less marked predominance of the one or the other.

*Phenomena related to the deactivating effect.*—The above explanation of the deactivating effect allows a better understanding of the following phenomena:

(a) Attention was drawn to deactivators by noting that mercaptobenzimidazole, marketed as an antioxidant, actually exerts an efficient protection without appreciably affecting the oxidizability of the vulcanizate. The deactivator can but slightly combat the oxidative scissions because of its low antioxidant power, but can combat degradation by the creation of new crosslinks. It is therefore easily understood why the absorption of a same quantity of oxygen is markedly less harmful than in the reference vulcanizates.

(b) It has already been stressed by Dufraisse<sup>30</sup> that when aging and oxidizability of vulcanizates accelerated with diphenylguanidine or litharge are compared, oxygen absorption seems less harmful for the second type. As the litharge concentration is relatively important (5-10%), it may be thought that a substantial portion remains after curing and can then create enough new links to act as a deactivator. The fact that the oxidation of these vulcanizates is much more detrimental at higher temperatures may be explained by different temperature coefficients, since oxidation and crosslinking are different reactions.

We should also pay attention to the work of Minatoya and Andō<sup>31</sup>, indicating that the addition of a small quantity of *m*-dinitrobenzene will give about the same results for aging resistance as the aldol- $\alpha$ -naphthylamine antioxidant taken as reference. We do not think that this compound is either a vulcanization "control," as suggested by these authors, nor is transformed into an antioxidant substance as suggested by others<sup>32</sup>, but that here again there is a possible after-cure crosslinking.

(c) The continuous relaxation measurements data indicate that the deactivator has but a small effect during vulcanization upon the initial structure of the network, provided care is taken to compare optimum-cured compounds. It is to be expected that for the same curing time this effect is reflected in mechanical properties, especially when using, as Shelton and Cox<sup>11</sup> did, mercaptobenzimidazole which has a much stronger action on vulcanization than the zinc salt. This explains why the theory suggested by these authors appeared credible. Although it is no longer satisfactory in the light of results given above, its main merit is in pointing out part of what we may now consider to be the real nature of the phenomenon.

(d) Better protection when using antioxidant and deactivator together, as well as differences noted in the case of various accelerators, are also logically explained. The antioxidant, by retarding the scissions, and the deactivator, by producing new crosslinks, are both contributing in maintaining the network so that their effects are effectively complementary. However, if the crosslinks created under the influence of the accelerator in the initial network are too weak, the deactivator will improve aging. Conversely, the deactivator is less useful when the accelerator can behave similarly by itself.

(e) Recent experiments by Zijp<sup>33</sup> have shown that a very large portion of mercaptobenzimidazole disappears during vulcanization and aging. Zijp thought, very aptly, that this was inconsistent with the peroxide-deactivation mechanism of our first theory, but did not say what became of mercaptobenzimidazole. From what we know of the transformation of mercaptobenzothiazole during vulcanization<sup>34</sup>, it is likely that dibenzimidazyl disulfide is formed. As it has been shown<sup>2</sup> that this product also acts as a deactivator, it is understandable that protection is maintained although mercaptobenzimidazole "disappears."

*Consequences related to general aspects of aging.*—On the basis of observations made in the course of this work and of the consequent conclusions, it seems that

we may go beyond the deactivating effect and examine certain more general aspects of aging.

It is known that vulcanizates prepared by using different accelerators, in the absence of any protective agent, age differently, and this has been related without any clear reasons to either the network structure or some antioxidant action of the accelerator (or of products produced during curing). Even if the different initial network structures do lead to different resistance to aging through different crosslink degradation, as confirmed by differences between continuous relaxation values, we may expect also that the abilities of accelerators to create new crosslinks during aging will play an important part. Consequently, the accelerators giving the best aging will be those which can after-cure to give resistant crosslinks, so that their action is related to the "deactivating" effect.

Such differences evidently affect the phenomena which occur during aging in the presence of a protective agent. We have expanded our ideas on this subject above. We should, however, mention that Haehl<sup>12</sup> has already drawn attention to the influence of accelerators. He thought his tests indicated that the protective mechanism in the presence of a deactivator was not the same when using diphenylguanidine as when using mercaptobenzothiazole. We have shown that the difference does not reflect a change of mechanism, but simply the relative importance of accelerator and deactivator effects.

We also see why it has not been possible to establish any relation between degradation and the quantity of absorbed oxygen when comparing the aging of either different vulcanizates protected by one and the same antioxidant, or one and the same vulcanizate containing different antioxidants. In the first case, the results are variably modified by the deactivating effect of the accelerator, inasmuch as it is able to repair part of the damaged caused by oxidation. In the second case, the effect apparently arises from the degree of deactivating power with which most antioxidants are endowed.

Another obscure point is that some antioxidants, efficient at normal temperatures, exhibit a decreasing effect when the temperature of test is increased, while others are considered to be endowed with a specific heat-resistance power. We also know that the classification of different compounds by order of aging resistance may vary considerably with the aging temperature. It seems that here again we may see an influence of the deactivating effect of the antioxidant, which does not act through the same mechanism as the antioxidant effect and might have a different temperature coefficient. This would be in line with the highly encouraging results on the heat resistance of deactivator systems obtained by Durou<sup>20</sup>.

Finally, it seems likely that such phenomena as reversion, the pro-oxidant effect, sun-checking, or development of tackiness are also regulated by the network structure and its resistance to degradation and that protection requires additional crosslinking. For example, it was shown by Haehl<sup>19</sup> that zinc mercaptobenzimidazolate is an excellent copper-inhibitor, and by Pinazzi and Mrs. M. Billuart<sup>35</sup> that nickel dibutylthiocarbamate, perhaps owing to its accelerator structure, protects rubber against light. We may also question whether such considerations do not actually explain certain apparently paradoxical results, such as the special behavior of protective agents in the case of vulcanizates prepared directly from latex<sup>36,37</sup>, or the fact that the products which protect raw rubber have no action on vulcanized rubber and vice-versa. It is possible that in the first case, part of the effect is due to the more or less marked

deactivating power of the accelerator as well as the action of natural protective agents. In the second case, the protection operates preferentially either against the scission of isoprenic chains or against the breaking of crosslinks.

### CONCLUSIONS

In order to better understand the complex phenomena related to aging, the two following propositions should be considered:

(a) Each type of vulcanizate has a particular type of network structure, with characteristics dependent on the number and nature of the crosslinks between the macromolecules. Thermo-oxidative degradation may have varying effects according to the network points which are preferentially attacked.

(b) The protection at present employed against the consequences of this degradation is based upon two different mechanisms, i.e., through the antioxidant effect, which retards the scission reaction, or through the deactivating effect, which helps to maintain the network by forming additional crosslinks.

If we also take into account the fact that each accelerator is able, as is the deactivator, to create specific new bonds by after-cure, we may suggest an explanation for some unexplained aspects of the related phenomena. From our results and the derived deductions ideas emerge, from which it should be possible to establish, by logic (instead of empirically) and by adaptation to each type of vulcanizate, some rules for the best protection with the present-known protective agents.

It should be noted that all preceding observations refer exclusively to the most widely used industrial practice, sulfur curing. However, the knowledge we now have of the deactivating effect mechanism has led us to think that it should also be possible, for vulcanizates produced with other vulcanizing agents, to find substances which will play the same part as our present deactivators, although of a totally different chemical composition.

As a matter of fact, the so-called deactivators are but slow-acting crosslinking agents, the new crosslinks resulting from either a mobilization of the unused vulcanizing agent in the vulcanizate or from a direct intervention of the deactivator. We therefore doubt whether their name, derived from the first, and inexact, explanation given for their action, is still justified. However, to change it we should have to evoke an after-crosslinking, a source of confusion with other current terms; moreover, a number of other wrong terms have been confirmed by use, for instance, the English "antioxidant"<sup>38</sup>. As these deactivators make degradation less active, their original name is perhaps not so inappropriate after all.

### SYNOPSIS

The mechanism of protection by the deactivating effect has been studied on the basis of data from continuous and discontinuous relaxation experiments on vulcanizates accelerated with mercaptobenzothiazole and with diphenylguanidine. It has been shown that the mechanism involves the formation of intermolecular crosslinks, which restore the damages due to the thermo-oxidative ruptures in the vulcanizate network. These intermolecular crosslinks are formed by the free sulfur present in the vulcanizates under the influence of the deactivator, which acts as a slow accelerator, as has been proved by free sulfur determinations carried out during aging. The resistance of these crosslinks to the thermo-oxidative degradation is specific for the deactivator; this allows for

interpretation of the more or less pronounced effect of the deactivator upon aging as a function of the nature of the accelerator used during vulcanization. This explanation of the deactivating mechanism gives not only a better understanding of the phenomena, but also presents new ideas for the general interpretation of aging of vulcanized rubber.

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## OZONE RESISTANCE OF NATURAL RUBBER VULCANIZATES

### PART I. APPARATUS FOR EXPOSURE AT LOW OZONE CONCENTRATION \*

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#### INTRODUCTION

As early as 1880, Bolas<sup>1</sup> demonstrated the detrimental effect of ozone on stretched rubber by exposing an inflated balloon to a stream of ozone. The balloon burst almost immediately. In 1885 Thompson<sup>2</sup> showed that ozone cracks rubber only if it is stretched.

Although ozone is present in the atmosphere in only minute quantities there is sufficient to attack rubber and to cause cracks to form perpendicular to the direction of applied stress. This phenomenon, cracking, must be distinguished from crazing, or sunchecking, in which the fissures run in random directions and form a network over the surface. The occurrence together of both cracking and crazing, when rubber vulcanizates are exposed to the atmosphere, has probably been the cause of some of the confusion in the early literature, even though Williams<sup>3</sup> and van Rossem and Talen<sup>4</sup> showed that only ozone causes cracking perpendicular to the direction of the stress and that ozone cracking and crazing are quite different phenomena.

As ozone must be considered a primary cause of the failure of rubber articles exposed to the atmosphere, it would be valuable to be able to predict the durability of vulcanized rubber and this would be possible if reliable ozone-testing results were available. The influence of various compounding ingredients on ozone resistance could also then be studied in the laboratory, and it would be possible to indicate compounding changes which would prolong the useful life of rubber vulcanizates.

#### APPARATUS DESCRIBED IN THE LITERATURE

During the last 30 years several types of ozone apparatus have been described. In 1931 Kearsley<sup>5</sup> developed an ozone apparatus which used a modified Smith ozone generator<sup>6</sup> to produce a concentration of one part in 50,000. In 1946 Crabtree and Kemp<sup>7,8</sup> concluded that such a concentration is too high for testing purposes and that  $25 \times 10^{-8}$  gives better correlation with service. They built an apparatus to work at this concentration which was measured by a special ozone-absorbing device. Accurate measurement of ozone at concentrations of the order of  $10^{-7}$  ml/ml is very difficult and it is not surprising that many methods have been suggested<sup>9,10,11,12,13,14,15</sup>. The most practicable

\* This work has been carried out since August 1952 under the supervision of Prof. Dr. A. van Rossem and has been published as a thesis for which the author was awarded the degree of Doctor of Technical Science (Delft) on 21st March, 1956. (Abstract, Summary of Current Literature 34, 213 (1956).) The article as reprinted here is from the *Transactions of the Institution of the Rubber Industry*, Vol. 34, pages 28-36 (1958). Parts II and III follow in this issue. (ICCR Class No. 64346.)

one for laboratory use is that described by Crabtree and Kemp<sup>7,8</sup>. Their apparatus, a version of which is recommended in ASTM D1149-54T, depends on the oxidation to iodine of a buffered solution of potassium iodide which is then titrated against sodium thiosulfate; and to correct for the evaporation of iodine, because of the large quantities of air which have to be used, a correction factor

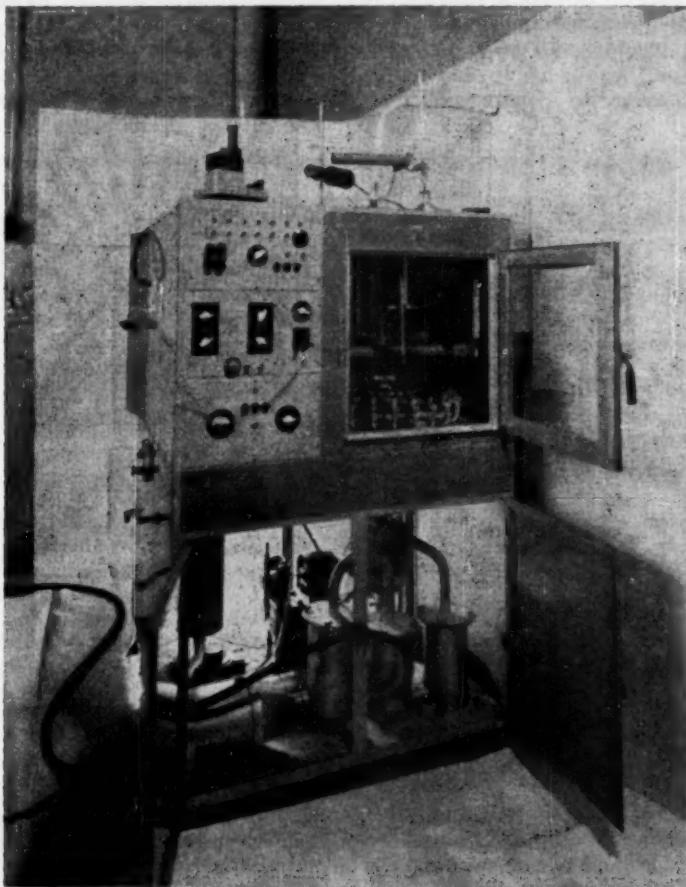


FIG. 1.—Front view of apparatus for static and dynamic testing of rubber vulcanizates exposed to constant ozone concentration.

of 10/9 is applied to correct the final result. This difficulty can also be avoided by adding a known quantity of  $\text{Na}_2\text{S}_2\text{O}_3$  to the KI solution and by determining the unreacted  $\text{Na}_2\text{S}_2\text{O}_3$  which is left. This method seems to prevent<sup>16,17</sup> some side reactions such as the formation of iodates and the destruction of ozone by OH ions, both of which can occur when buffered aqueous solutions are used.

Ford and Cooper<sup>18</sup> have described an apparatus in which the ozone con-

centration is kept constant automatically. They do this by passing a measured quantity of the ozonized air through a Crabtree-and-Kemp absorption apparatus into which a constant amount of  $\text{Na}_2\text{S}_2\text{O}_3$  solution is titrated by a metering system such as in Figure 2. At the right concentration this amount of  $\text{Na}_2\text{S}_2\text{O}_3$  just neutralizes the generated iodine. If the ozone concentration changes, the electrometric titration system activates a mirror galvanometer which, by means of a photocell and amplifier, puts in or out of circuit an auxiliary ozone generator. The apparatus of Ford and Cooper enables rubber to be tested under both

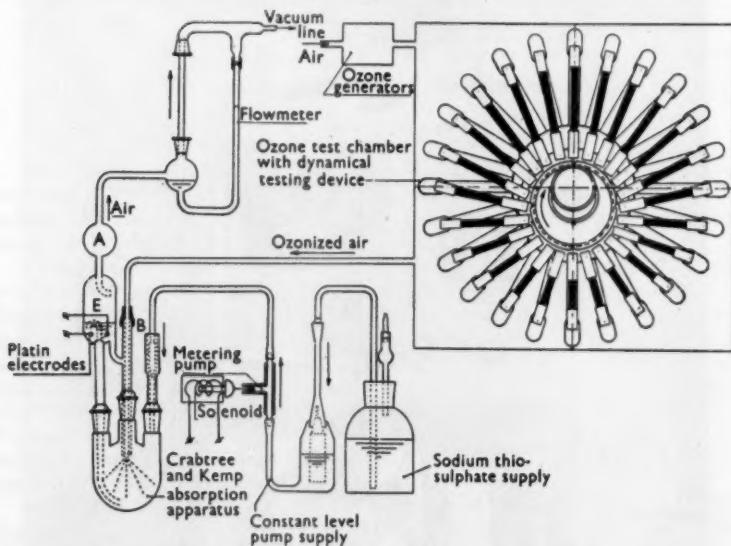


FIG. 2.—Titration system and dynamic testing mechanism.

static and dynamic conditions over a wide range of ozone concentrations at a fixed temperature and humidity; a system of light sources allows different light spectra for weathering tests.

#### APPARATUS AT THE RUBBER RESEARCH INSTITUTE, T.N.O.

This apparatus (Figure 1) combines the principles of Crabtree and Kemp<sup>7</sup> with some of the improvements suggested by Ford and Cooper<sup>18</sup>, but it has been built for ozone testing alone and not for weathering.

The apparatus meets the following requirements.

(a) Ozone concentration can be varied between 5 and  $50 \times 10^{-8}$  ml/ml but, as recommended by Crabtree and Kemp and by ASTM D1149-54T,  $25 \times 10^{-8}$  is the concentration most often used. The choice of this concentration has been supported by our own experiments.

(b) Ozone concentration is kept constant automatically to allow for losses of ozone.

(c) Testing temperature is controlled because rate of crack-growth increases with temperature<sup>5, 8, 19, 20</sup>.

(d) Provision is made for testing under both static and dynamic conditions.  
(e) There is no control of humidity because it seems that this does not effect ozone cracking<sup>15,18,21</sup>, but only influences "frosting"<sup>22,23</sup>.

(f) Because the apparatus is intended for ozone exposure and not for weathering, no light sources are included, nor water-sprays to imitate rainfall.

(g) Because spectrographic and other methods for determining ozone concentration seem less suitable<sup>12,13</sup>, the Crabtree-and-Kemp absorption method is used. This is reproducible within 5 per cent for vessels of different capacity<sup>7,8</sup>, and reproducibility is improved even more by using the same vessel each time and by adopting the continuous titration system of Ford and Cooper<sup>18</sup>, so that variations in concentration can be corrected automatically by an auxiliary ozone generator.

To meet these requirements the apparatus incorporates the following:

- (i) A titration system with a metering pump-driven mechanism.
- (ii) An ozone-absorption device with electrometric titration (deadstop endpoint) to show the amount of generated iodine as a deflection of a mirror galvanometer.
- (iii) A photocell, activated by the light reflected by the galvanometer mirror, and an amplifier to operate the auxiliary ozone generator.
- (iv) An air-circulation system with air-purifying towers, ozone generators and ozone cabinet.
- (v) Temperature control for the ozone cabinet.
- (vi) Mechanism for testing rubber under both static and dynamic conditions.

#### DETAILED DESCRIPTION OF THE APPARATUS

*Titration system (Figure 2).*—This incorporates a plunger-type metering pump driven by an electronic timing device. If the working conditions are carefully chosen the timing device and the pump will give an overall reproducibility of 98.5 per cent.

The capacity of the pump is determined by passing through the ozone absorption apparatus 5000 ml of air per minute with an approximate ozone concentration of  $25 \times 10^{-8}$  ml/ml. This corresponds to  $1.1 \times 10^{-7}$  gram eq. of ozone. An equivalent amount of  $\text{Na}_2\text{S}_2\text{O}_3$  is added: 110 mg/min for a  $\text{Na}_2\text{S}_2\text{O}_3$  solution of  $10^{-6}$  g eq/ml. Thus, if each charge delivered by the pump is 30 mg, 4 charges/minute will be required. To cover a wide range of ozone concentrations a pump is needed which can supply a wide range of charges. The pump used will give charges between 10 and 45 mg/min.

The ozone concentration can be changed either by altering the charge of the pump or by varying, with the timing device, the number of charges per minute. The timing device is so constructed that the pump valve is closed during the rest period at the end of each half-stroke of the pump.

*Ozone-absorption device and electrometric titration (Figure 2).*—The ozone-absorption device is as Crabtree and Kemp<sup>7</sup> described except that two platinum electrodes have been inserted at "E" in Figure 2 to measure the concentration of iodine by the electrometric method of Faulk and Bawden<sup>24</sup> using the dead-stop endpoint. A constant potential difference, which can be adjusted with a potentiometer to between 15 and 25 mv, is applied between the platinum electrodes.

When the ozone concentration is right no iodine or thiosulfate ions are

present and a mirror galvanometer in circuit with the electrodes is not deflected. Any change in the ozone concentration results in a deflection of the galvanometer.

*Photocell and amplifier to operate the auxiliary ozone generator.*—The light reflected by the galvanometer mirror falls on a photocell. When the galvanometer is deflected the changed signal from the photocell is passed to a one-stage amplifier which operates a relay to switch the auxiliary ozone generator on or off. The circuit is shown in Figure 3.

*Air-purifying system, ozone generators and ozone cabinet.*—The incoming air is filtered through active charcoal and finely-divided alumina to prevent oil droplets and nitrogen oxides from entering the cabinet. If complete absence

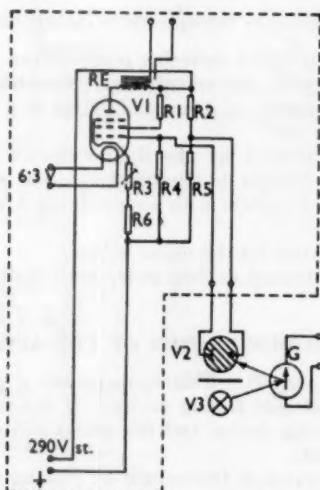


FIG. 3.—Photocell—amplifier circuit.

R1	3, 9 k $\Omega$	V1	EL 41
R2	1 M $\Omega$	V2	3533
R3	5 k $\Omega$	V3	4 v, 0.5 a, electric bulb
R4	100 M $\Omega$	G	Galvanometer
R5	470 k $\Omega$	RE	DC relay, working conditions:
R6	1 k $\Omega$		opening at 6 ma, closing at 9 ma

of ozone is required one of the two towers otherwise filled with alumina is filled instead with cotton wool. The filtered air then passes into an aluminum chamber which contains the main and auxiliary ozone generators.

The main ozone generator is a Hanovia Safe-t-Air lamp, 93-A-1. The ultraviolet light emitted by this lamp, and hence the output of ozone, is controlled by varying the voltage across the primary of the transformer which supplies the lamp. The auxiliary ozone generator is an ordinary neon bulb surrounded by an earthed aluminum gauze; the electrodes of the bulb are connected to a 3500 v AC supply and a 47 k $\Omega$  resistance is included in the circuit.

The ozonized air is then passed through a tower filled with glass marbles and into the ozone cabinet through three vents in the double bottom of the cabinet. The upper plate of this double bottom, which is 1 cm above the lower

plate, is also perforated, but none of the holes in it are opposite the three in the lower plate through which the ozone enters. The sides of the upper plate are 1.5 cm smaller than the sides of the ozone cabinet. A fan which circulates the ozonized air around the testpieces completes the system for insuring uniform ozone concentration throughout the cabinet. Air is removed from the cabinet through a double ceiling whose lower plate is smaller than the cabinet. The dimensions of the cabinet are 50 × 50 × 50 cm; this gives sufficient space for the simultaneous testing of 30 specimens statically and 24 dynamically.

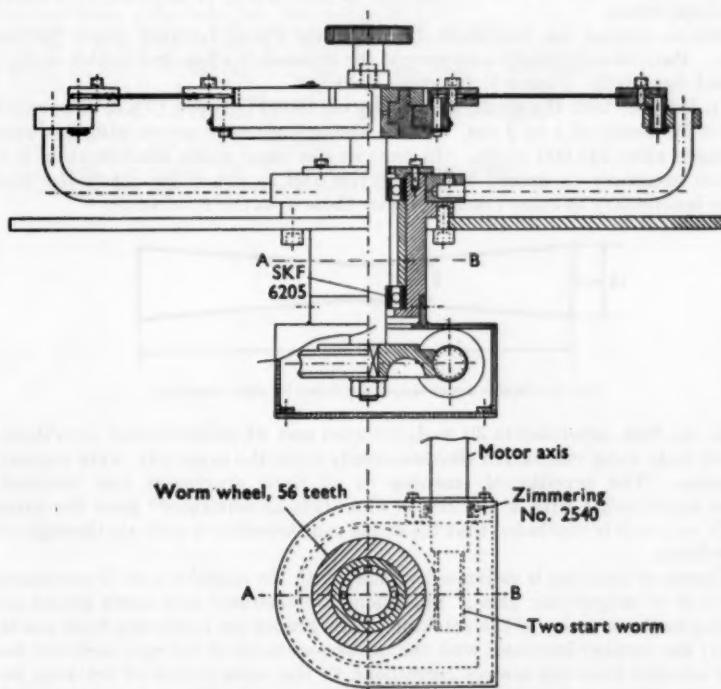


FIG. 4.—Dynamic testing mechanism.

Temperature in the cabinet is controlled automatically. For testing at room temperature the ozonized air is heated before entering the cabinet. Higher temperatures are obtained with 250 w heating coils in the walls of the cabinet. Temperature is controlled within  $\pm \frac{1}{4}^{\circ}$  C over the range between 20° and 100° C.

*Static and dynamic testing mechanism.*—Two racks can be mounted in the ozone cabinet to hold 30 dumbbells under static elongation in six groups of five; the five specimens of each group are given the same elongation.

The mechanism for testing 24 dumbbells under dynamic conditions is illustrated in Figures 2 and 4. The elongation cycle is produced by rotating a double eccentric; the maximum elongation in the cycle can be varied between 0 and 100 per cent by adjusting the positions of the two eccentrics relative to each

other. The moving ends of the dumbbells are clamped to a gliding bronze ring which surrounds the outer eccentric and the other ends are clamped to a stationary ring mounted concentrically with the axis of rotation.

#### EXPERIMENTAL PROCEDURE

Dumbbell specimens are cut from slabs which have been vulcanized between highly-polished stainless-steel plates. The thickness of the slabs is controlled within  $2.00 \pm 0.05$  mm to reduce stress variation among the elongated specimens.

Before cutting the dumbbells the slabs are stored between paper for ten days. Parallel-sided testpieces are cut for dynamic testing and double wedge-shaped dumbbells (Figure 5) for static testing.

In dynamic tests the strain is normally oscillated between 15 and 25 per cent with a frequency of 1 to 2 cps. In the absence of ozone no cracking has been produced after 225,000 cycles. In tests at the usual ozone concentration it is seldom necessary to exceed 150,000 cycles and so it can be concluded that ozone is necessary to cause cracking under these dynamic conditions.

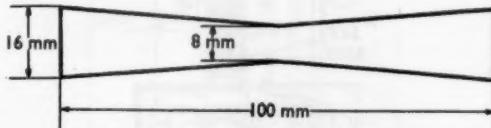


FIG. 5.—Double wedge-shaped dumb-bell for static exposure.

In the first experiments 30 wedge-shaped and 24 parallel-sided dumbbells, all cut from slabs vulcanized simultaneously from the same mix, were exposed to ozone. The severity of cracking in all these specimens was identical. Later experiments with a number of Goodrich ozonometers<sup>26</sup> gave the same result, and so it is concluded that the ozone concentration is uniform throughout the cabinet.

Degree of cracking is estimated visually with the naked eye or, if necessary, with a  $5\times$  magnifying glass. Specimens are classified into seven grades according to the severity of the cracking. The grades are numbered from one to seven; the number increases with the ozone resistance of the specimen but the same number does not always correspond to the same degree of cracking because classification into these seven grades is varied with each series of vulcanizates tested. For instance, when testing a series of compounds containing substituted *p*-phenylenediamines, which give good protection against ozone, more severe standards are set for the higher grades than when testing groups of less-resistant stocks. When, in later sections of this paper, the results of such tests are given, typical photographs will be produced to indicate these differences.

#### SUMMARY

An apparatus is described for evaluating the cracking resistance of rubber specimens exposed under static or dynamic conditions to ozone concentrations between 5 and  $50 \times 10^{-8}$  ml/ml of air. Ozone concentration is kept constant automatically however much is destroyed at the walls of the cabinet or at the surfaces of the rubber testpieces. Temperature can be regulated between 20° and 100° C.

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## PART II. INFLUENCE OF FILLERS AND WAXES \*

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The influence on ozone cracking of vulcanized natural rubber of the following classes of compounding ingredients has been investigated.

- (a) Carbon blacks,
- (b) White reinforcing fillers,
- (c) Paraffin waxes.

Different types of these ingredients were added to a base mix, and ozone-cracking resistance was evaluated at one time of cure in each case after a preliminary investigation had shown differences in curing time to have little effect. The base mix consisted of RSS 100, zinc oxide 5, stearic acid 1, sulfur 2, 2-benzothiazolyl N-cyclohexyl sulfenamide, 1.

### INFLUENCE OF CURING TIME

Because the literature contains contradictory statements<sup>1,2,3,4,5</sup>, about the effect of curing time on ozone cracking, the base mix used in these experiments was tested after curing for 15, 17½, 20, 22½, 25, 30 and 40 minute sat 142° C. No differences in ozone cracking were observed among these vulcanizates when they were exposed at 23° C or at 55° C, but at 40° C severity of cracking tended to increase with curing time. Even then the effect was negligible for small changes about the optimum cure, so in all later experiments testpieces were given optimum cure as nearly as possible.

### INFLUENCE OF REINFORCING INGREDIENTS

Smith and Gough<sup>6</sup> have shown that the rate of growth of a crack depends on the stress concentrations at its ends. It would be reasonable to suppose that such stress concentrations will be greater in higher-modulus vulcanizates and that crack growth will then be more rapid.

To investigate this a comparison has been made of a number of blacks ranging from "soft" blacks such as Thermax A and P33, to high-modulus blacks such as Philblack A, Philblack O and Statex 125. Some reinforcing silicas have also been included which give moduli at 100 per cent elongation of the same order (20 to 25 kg/cm<sup>2</sup>) as carbon blacks.

*Carbon black.*—Popp and Harbison<sup>7</sup> examined the joint effect on black-loaded GR-S vulcanizates of ultraviolet light and of the ozone that it generates. They concluded that the degree of cracking varied little among different types of carbon black. But, as the ozone concentration during their experiments was unknown and any effect caused by the UV light itself could not be distinguished from the effect of the ozone, it was thought necessary to examine the ozone effect alone.

Forty parts by weight of each of the carbon blacks was added to 109 parts

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TABLE I  
PHYSICAL PROPERTIES OF BLACK-LOADED VULCANIZATES

Carbon black	Optimum cure time, min	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %	Shore hardness	Modulus at elongations of						
					100	150	200	250	300	350	400
CK3	15	338	630	60	15	33	55	84	115	148	190
CK4	15	344	620	60	15	30	51	75	110	142	178
Statex 125	15	331	565	65	23	41	67	103	139	175	218
Statex R	10	313	545	62	19	39	64	91	124	159	197
Statex K	15	338	620	58	19	31	50	75	106	137	173
Kosmos 40	15	291	546	62	17	30	54	85	120	155	191
Kosmos 60	15	309	570	61	18	27	60	89	122	158	196
Philiblack E	15	354	590	62	18	37	70	100	140	178	210
Philiblack O	15	326	528	62	24	43	73	106	145	187	229
Philiblack A	15	293	480	55	32	54	95	129	164	203	234
Thermax A	15	262	596	49	—	16	28	44	66	98	132
P33	15	296	670	51	—	—	26	37	52	70	104

of the base mix and testpieces were given their optimum cure at 142° C. The types of black used, the cure times and the physical properties of the vulcanizates are shown in Table I.

Double wedge-shaped specimens were exposed statically and parallel-sided specimens dynamically at three temperatures, 23°, 40° and 55° C, to an ozone concentration of  $25 \times 10^{-8}$  ml/ml.

TABLE II  
PHYSICAL PROPERTIES OF VULCANIZATES LOADED WITH WHITE FILLERS

Filler	Optimum cure time, min	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %	Shore hardness	Modulus at elongations of					
					50	100	150	200	250	300
Silteg AS5	15	237	550	60	14	22	31	41	52	109
Silteg AS7	15	246	560	59	14	23	32	40	54	183
Ultra Silteg VN3*	25	198	570	58	12	20	28	35	44	149
Hisil	35	228	570	58	13	22	30	41	53	181
Silene EF	15	210	545	56	14	24	33	42	53	176
Hakuunka	15	270	600	54	11	19	25	31	40	167

\* Alkaline grade, no longer available.

In spite of the differences in modulus (Table I) between these stocks, no appreciable differences in cracking were observed among the testpieces exposed statically, among those exposed dynamically, or among double wedge-shaped dumbbells exposed outdoors at elongations between 15 and 25 per cent.

*Inorganic reinforcing fillers.*—Several inorganic reinforcing fillers were compared also at 40 parts loading. These are listed in Table III together with their optimum times of cure and physical properties.

There were appreciable differences in the degree of cracking; these are graded in Table III.

TABLE III  
OZONE CRACKING OF VULCANIZATES LOADED WITH WHITE FILLERS

Filler	Static tests			Dynamic tests		
	23° C	40° C	55° C	23° C	40° C	55° C
Silteg AS5	3	1	3	3	3	3
Silteg AS7	3	2	3	4	3	3
Ultra Silteg VN3	2	4	6	2	3	3
Hisil	3	4	4	3	3	4
Silene EF	3	3	3	5	2	4
Hakuunka	3	3	4	6	5	5

TABLE IV  
PHYSICAL AND CHEMICAL PROPERTIES OF WAXES

Wax	Supplier	Molecular weight	Melting point	Penetration number	Refractive index	Straight chains, %	Side chains, %
<b>Sunproof</b>							
<b>Sunproof Super</b>	Naugatuck Chem.	500	66-67	9-10	1.4317	73	27
<b>Sunproof 713</b>	Naugatuck Chem.	850	69-70	8-9	1.4378	49	51
<b>Sunproof Improved</b>	Naugatuck Chem.	550	68-71	8-9	1.4322	71	29
<b>Sunproof Jr.</b>	Naugatuck Chem.	525	65-67	6-7	1.4324	70	30
<b>Halozone</b>	Du Pont de Nemours	475	58-59	10	1.4263	95	5
<b>Solnolite</b>	Witco Chemical Co. Ltd.	550	69	8	1.4327	69	31
<b>Okerin 444</b>	Astor Boisselier and Lawrence	450	66-68	11	1.4262	96	5
<b>Okerin 587</b>	Astor Boisselier and Lawrence	600	69-71	7-8	1.4330	68	32
<b>Okerin 812</b>	Astor Boisselier and Lawrence	650	77	20	1.4444	22	78
<b>Isocerine 1016</b>	Schliemann	650	70-72	11-12	1.4363	55	45
<b>Isocerine 1860</b>	Schliemann	550	80-81	66-67	1.4419	32	68
<b>Isocerine 1887</b>	Schliemann	550	68-71	20	1.4331	67	33
<b>Antilux</b>	Rheinchemie	650	82-84	32	1.4419	32	68
<b>Fortex wax</b>	Bischoff	400	61-64	11-12	1.4342	62	38
<b>Indonesian semirefined paraffin wax</b>	Was de Wit	775	91-92	3	1.4419	32	68
<b>Ozokeriet</b>	Was de Wit	425	57-60	10-14	1.4244	100	0
<b>Ceresine</b>	Was de Wit	525	79-80	8	1.4268	75	25
<b>Microwax PA72</b>	Was de Wit	425	55	10	1.4240	94	6
<b>Rubberwax 32000</b>	Was de Wit	725	81	16-17	1.4442	22	78
<b>Montan wax Riebeck</b>	Was de Wit	550	79-80	37-38	1.4422	42	58
<b>Microcrystalline wax</b>		85-86	0-1				
white	Shell Holland	750	78-79	19-20	1.4422	31	69
yellow	Shell Holland	575	69	55-58	1.4448	20	80
brown	Shell Holland	575	72-73	10	1.4343	63	37
	Jonk	550	64-65	12-14	1.4362	59	41
<b>Jonk 11586</b>							
<b>Jonk 11587</b>							

The best results under dynamic conditions are obtained with Hakuenka, which is a calcium carbonate coated with stearic acid. Under static conditions, particularly at 40°C, vulcanizates loaded with Silteg AS5 and AS7 have the lowest ozone resistance. Unlike the carbon blacks, these materials give different levels of ozone resistance, even though there are smaller differences between the moduli of their stocks than there are among the black-loaded vulcanizates.

#### PARAFFIN WAXES

Paraffin waxes are commonly used as protective agents against ozone attack. In 1956 Shepard, Krall and Morris<sup>1</sup> showed that paraffin waxes, especially purified montan wax, gave some protection against ozone, though vaseline and vegetable oils gave none. Van Rossem and Talen<sup>2</sup> and, later, Crabtree and Kemp<sup>3</sup> showed that the results obtained at normal atmospheric ozone concentrations differed from those at much higher concentrations. Crabtree and Kemp<sup>3</sup> also investigated the influence of temperature on stocks containing wax and concluded that at high temperatures the wax bloom is reabsorbed by the rubber and that at low temperature the wax bloom is brittle. Attempts to reduce this brittleness by mixing vaseline or mineral oil with the wax made the protection against ozone worse still.

A wax bloom must have the following properties if it is to provide adequate protection against ozone.

- (a) The wax must be slightly soluble in the rubber at room temperature;
- (b) The bloomed layer must be flexible;
- (c) Adhesion between the bloomed layer and the rubber surface must allow flexing without flaking;
- (d) Moderate elongation should not break or crack the wax layer.

Hence the protection provided by a wax depends on its physical and chemical properties.

The flexibility of the bloom depends on its thickness; this can be measured directly with the aid of a microscope or, better still, by the method of Best and Moakes<sup>4</sup> in which a known area of the surface is swabbed with a piece of cotton wool soaked in a solvent for the wax and the wax is extracted and weighed. This has shown that the thickness of the bloom increases considerably in the first few days but that after that the rate of migration to the surface becomes less.

Different waxes migrate to the surface at different rates. Microcrystalline waxes migrate more slowly than normal paraffins and their bloomed layers are more flexible and so give better ozone protection. An indication of the crystal size can be obtained by heating a 10 per cent solution of the wax in benzene to between 80° and 110° C and pouring a drop of the solution on a microscope slide. The growth and size of the wax crystals can be observed with a microscope and comparisons made between different waxes. In this way it has been found that by adding only small quantities of microcrystalline wax to normal paraffin wax, the size of the crystal needles is greatly altered. Plastics such as polyethylene have the same effect; addition of between  $\frac{1}{2}$  and 1 per cent is sufficient to prevent the formation of large wax crystals.

*Experimental.*—A number of waxes with different physical and chemical properties was chosen to be mixed into natural rubber vulcanizates. The following properties of these waxes were determined.

- (a) Molecular weight estimated from the depression of the melting point of camphor;
- (b) Melting point by the Ubbelohde method;
- (c) Penetration number—the penetration, in units of 0.1 mm, of a standard needle after 5 seconds under a load of 100 g at 25° C;
- (d) Refractive index measured with an Abbe refractometer;
- (e) Number of side chains, both aliphatic and aromatic, determined by cocrystallization with urea.

Approximate values of these properties are shown in Table IV.  
Each wax was mixed to the following formulae:

	A	B	C
Base mix	109	109	109
Thermax A	—	40	—
Hakukenka	—	—	40
Wax	3	3	3

Specimens were vulcanized at 142° C to give optimum tensile strength and were exposed for 30 hours under both static and dynamic conditions at 23° and 40° C in an ozone concentration of  $25 \times 10^{-8}$  ml/ml. Ozone cracking results are shown in Table V.

To give a simplified classification of the waxes according to the protection

TABLE V  
OZONE-CRACKING RESULTS OF VULCANIZATES CONTAINING WAX

Wax	Static tests Mixing temp., °C						Dynamic tests Mixing temp., °C						Effective value	
	A		B		C		A		B		C			
	23	40	23	40	23	40	23	40	23	40	23	40		
Group I														
Sunproof 713	7	7	3	7	7	7	3	2	3	2	3	3	38	
Sunproof Improved	7	7	3	6	7	7	3	2	3	1	3	3	37	
Sunproof Super	6	7	3	7	6	7	3	3	3	2	4	1	36	
Jonk 11586	6	7	3	7	6	7	1	1	2	1	3	3	36	
Group II														
Sunproof Jr.	6	7	5	3	5	6	2	3	3	2	3	2	32	
Sunproof	6	7	3	1	6	7	2	2	3	2	4	2	30	
Helizones	7	7	3	1	6	6	2	2	2	1	3	3	30	
Okerin 444	4	1	6	6	7	6	3	2	2	2	4	2	30	
Jonk 11586	5	4	3	7	5	6	2	1	3	1	3	3	30	
Indonesian Semirefined paraffin wax	7	2	7	5	6	6	3	3	3	4	3	4	29	
Okerin 812	5	7	3	1	5	6	2	3	2	2	3	2	28	
Isocerine 1860	5	2	3	3	6	6	2	3	4	4	3	3	25	
Group III														
Shell brown	7	7	3	3	2	2	2	2	4	5	5	4	24	
Sunolite	5	5	1	1	5	6	2	2	3	2	3	3	23	
Fortexwax	2	7	3	1	2	5	4	1	4	4	5	2	21	
Isocerine 1016	5	2	2	2	4	3	2	3	4	3	3	2	18	
Ceresine	5	2	3	4	2	2	3	3	4	3	4	3	18	
Antilux	6	2	2	3	2	2	3	3	3	3	3	2	17	
Microwax PA 72	5	1	3	2	3	3	—	3	5	3	4	1	17	
Okerin 587	4	1	2	2	4	3	4	4	4	3	4	1	16	
Ozokeritet	5	1	3	4	2	1	3	3	4	4	4	4	16	
Montan wax Riebeck	2	2	4	3	1	2	4	3	4	4	4	3	14	
Shell white	3	5	2	2	3	1	*	3	*	3	4	3	14	
Shell yellow	4	1	3	2	2	2	*	3	*	4	3	3	14	
Isocerine 1887	4	1	3	2	2	2	3	3	4	4	4	3	13	
Rubberwax 32000	3	1	3	3	3	1	3	3	4	4	4	2	13	
Control	1	1	3	3	1	2	4	4	4	4	6	5	11	

\*Broken in the grip or loosed by the grip.

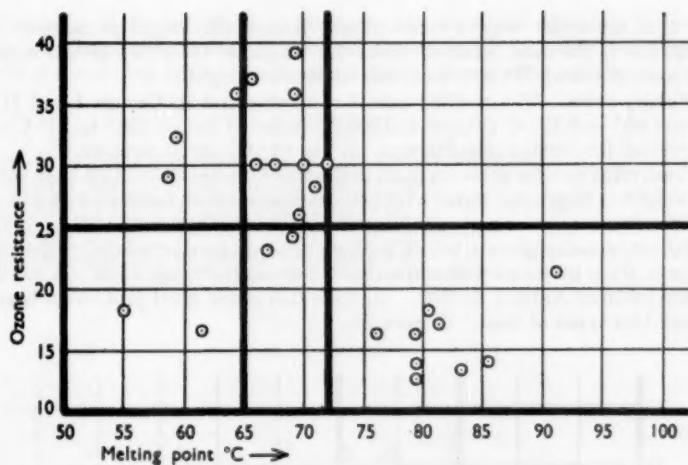


FIG. 1.—Relationship between melting point and ozone resistance.

they give against ozone the grade numbers in Table V for all the static tests on each wax were totalled to give an "effective value" which increases with the degree of ozone resistance imparted to the vulcanizates. This allowed the waxes to be grouped as they are in Table V.

These effective values were compared with the measured physical and chemical properties of the waxes to see which were related to their ozone protecting ability.

**Molecular weight.**—The waxes in Group I have molecular weights, 550, 525, 850 and 550, and in Group II, 475, 500, 550, 600, 575, 425, 650 and 550. It is

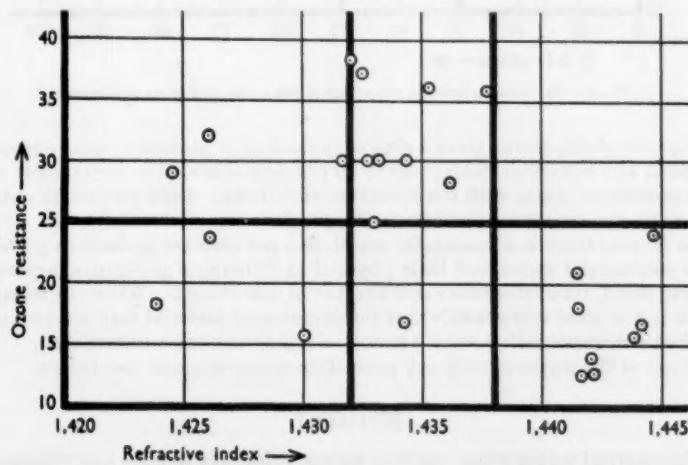


FIG. 2.—Relationship between refractive index and ozone resistance.

clear that molecular weight is not closely linked with ozone protection. Although 550 is the most common molecular weight in these two groups some of the waxes in Group III also have this molecular weight.

*Melting point.*—The melting points of most waxes in Groups I and II are between 65° and 72° C (Figure 1) though Sunproof Junior (58° to 59° C) and semirefined Indonesian paraffin wax (57° to 60° C) are exceptions.

*Penetration number* gives no more indication of ozone protection than molecular weight. In general waxes with penetration numbers between 6 and 14 give good results.

*Refractive index* gives a better indication of protective power. Good protection is given by waxes with refractive indexes in the range 1.432 to 1.438 with the exception of Antilux (1.434). Outside this range good protection is given by only two types of wax. (Figure 2).

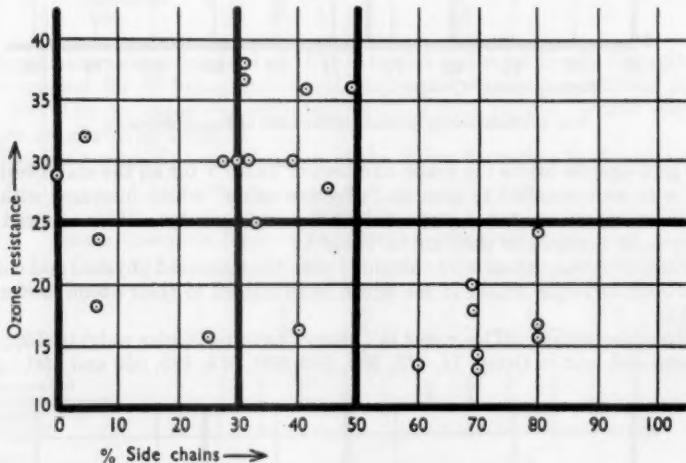


FIG. 3.—Relationship between percentage of side chains and ozone resistance.

*Number of side chains* gives a similar indication of protective power to melting point and refractive index. 30 to 50 per cent side chains corresponds with good protection, again with the exception of Antilux. Only two waxes outside this range also give good protection (Figure 3).

In general there is a reasonable correlation between the protective power of these commercial waxes and their physical and chemical properties, especially melting point, refractive index and number of side chains. When the relationship is not so good it is possible that the commercial material may not be a pure wax but a mixture with a small amount of a polymer or an antioxidant.

None of the waxes affords any protection under dynamic conditions.

#### SUMMARY

Commerical waxes whose melting points, refractive indexes and numbers of side chains are within the ranges described seem likely to give good ozone pro-

tection under static conditions. All waxes lead to worse cracking under dynamic conditions than if none had been included and it is clearly better to use no wax if the rubber is likely to be submitted to intermittent stretching.

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## OZONE RESISTANCE OF NATURAL RUBBER VULCANIZATES

### PART III. INFLUENCE OF ACCELERATORS AND ANTIOXIDANTS \*

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#### ACCELERATORS

The influence of accelerators on the ozone resistance of natural rubber vulcanizates was investigated by Shepard, Krall and Morris<sup>1</sup>, who found that diphenylguanidine, triphenylguanidine and methylene-*p*-toluidine had no effect on ozone resistance, but tetramethylthiuram disulfide, when used as a vulcanizing agent, gave good resistance.

Van Rossem and Talen<sup>2</sup> found that 2-mercaptopbenzothiazole (MBT), dinitrophenyl-2-thiobenzothiazole with diphenylguanidine (Ureka), tetra-methylthiuram disulfide (Methyltuads) or diphenylguanidine (DPG) had no influence on ozone cracking in normal rubber-sulfur mixes.

Little further information can be found in the literature. In the present work the accelerators listed in Table I have been investigated.

The following base mix was used throughout.

RSSI	100
Zinc oxide	5
Stearic acid	1
P33 carbon black	3

To this base mix accelerator and sulfur were added in the quantities listed in Table II, which also shows the vulcanization temperature used, the optimum cure time and the physical properties of each vulcanize.

Specimens were exposed to an ozone concentration of  $25 \times 10^{-8}$  ml/ml under both static and dynamic conditions for 30 hours at 23°, 40° and 55° C. Doublewedge-shaped specimens were used for static tests and were stretched to elongations between 15 and 25 per cent. Rectangular dumbbells were used for dynamic tests and were oscillated between 0-15 per cent elongation with a frequency of 1-1½ cps. Degrees of cracking was graded as before, the grade number increasing with the ozone resistance of the vulcanizate. The results are given in Table III and are illustrated in Figures 1 to 8.

The following comments summarize the behavior of each group of accelerators.

*Guanidines* gave little protection, especially under static conditions.

*Dithiocarbamates* generally gave better protection than guanidines, especially under static conditions. Best of all was sodium diethyl dithiocarbamate.

*Thiazole derivatives*, except 2-mercaptopbenzothiazoline, gave better protection than the dithiocarbamates.

\* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 34, pages 86-100 (1958). See the preceding paper, this issue, for Part II. (ICCR Class No. 6323153.)

*Condensation products*, especially under dynamic conditions, gave less protection than the guanidine accelerators.

Of the *nonclassified accelerators*, 2-mercaptoimidazoline gave less protection than Vulcafor F, which gave about the same as the guanidines.

TABLE I  
ACCELERATORS

Chemical name	Trade name or abbrev.
<b>GROUP I. Guanidines</b>	
Diphenylguanidine	DPG
Di-o-tolylguanidine	DOTG
Triphenylguanidine	TPG
Orthotolyl biguanidine	Vulkacit 1000
<b>GROUP II. Dithiocarbamates</b>	
Zinc dimethylidithiocarbamate	Methyl Zimate, ZnDMDC
Zinc ethylphenyldithiocarbamate	Vulkacit P extra N
Zinc diethylidithiocarbamate	Ethyl Zimate, ZnDEDCC
Zinc dibutylidithiocarbamate	Butyl Zimate, ZnDBDC
Zinc N-pentamethylenedithiocarbamate	Pipazate, ZnPDC
Piperidinium N-pentamethylenedithiocarbamate	Pip-pip
Sodium diethylidithiocarbamate	Vulcafor SDC
<b>GROUP III. Thiazole derivatives</b>	
2-Mercaptobenzothiazole	Captax, MBT
2-Benzothiazoyl disulfide	Altax, MBTS
N-Cyclohexyl-2-benzothiazoyl sulfenamide	Santocure
2-Mercaptothiazoline	2MT
<b>GROUP IV. Condensation products</b>	
Butyraldehyde-aniline condensation product	Accelerator 808
Hexamethylenetetramine and phthalic anhydride	Vulkacit H
Triethyltrimethylenetriamine	Trimene base
Trimene base and stearic acid	Trimene
Crotonaldehyde-ammonia condensation product	Vulkacit CT
Acetaldehyde-aniline formaldehyde condensation product	A19
<b>GROUP V. Nonclassified</b>	
2-Mercaptoimidazoline	NA22
Di-2-benzothiazoyl disulfide and diphenylguanidine	Vulcafor F
<b>GROUP VI. Thiuram derivatives</b>	
Tetramethylthiuram monosulfide	Thionex, TMTM
Tetramethylthiuram disulfide	Methyl Tuads, TMTD
Tetraethyl thiuram disulfide	Ethyl Tuads, TETD
Dipentamethylene thiuram tetrasulfide	Tetrone A, DPTD

*Thiuram derivatives* when used as accelerators gave static ozone resistance which increased with test temperature. Protection at 23° C was poor compared with the thiazole derivatives, but was better at 40° and 55° C.

*Thiuram derivatives* used as vulcanizing agents gave good resistance under both static and dynamic conditions, especially dipentamethylene thiuram tetrasulfide.

Table II shows considerable variation in modulus at 50 per cent, 100 per cent and 500 per cent among the various accelerators, but this variation in modulus seems not to be connected with ozone resistance.

TABLE II  
ACCELERATOR AND SULFUR LOADING

Accelerator	Sulfur loading	Optimum cure time, mins.	Cure temp., °C	Tensile strength, kg./cm. <sup>2</sup>	Elongation at break, %	Modulus at		
						50%	100%	500%
<b>Group I. Guanidines</b>								
DPG	2	30	147	316	820	37	3.0	6.3
DOTG	2	30	147	334	725	38	3.6	6.7
TPG	2	25	147	304	905	27	2.2	3.6
Vulksit 1000	2	25	147	304	845	40	4.0	6.0
<b>Group II. Dithiocarbamates</b>								
Methyl Zimate	2	20	135	299	780	41	3.9	6.9
Vulkacit P extra N	2	15	125	347	770	44	4.4	43
Ethyl Zimate	2	20	135	291	730	43	4.7	65
Butyl Zimate	2	15	142	283	825	37	3.2	57
Pipasate	2	20	135	304	775	40	4.2	31
Pip-pip	2	15	125	384	710	48	7.3	45
Vulksit SDC	2	7	118	340	765	42	6.0	123
<b>Group III. Thiazole derivatives</b>								
Capax	2	15	147	244	890	35	3.5	5.5
Altax	2	25	147	298	860	38	3.4	5.2
Santocure	2	30	147	366	715	43	5.6	33
2MT	2	35	147	175	860	35	2.6	84
<b>Group IV. Condensation products</b>								
Accelerator 808	2	25	142	260	725	41	4.4	7.0
Vulkacit H	2	25	142	174	920	31	2.3	56
Trinene base	2	30	147	367	765	43	5.0	—
Trinene	2	40	147	300	805	40	8.6	86
Vulkacit CT	2	25	147	299	820	38	3.8	42
A19	2	25	147	174	890	31	6.0	41
<b>Group V. Nonclassified</b>								
NA22	2	15	142	312	825	40	3.6	48
Vulksit F	2	20	142	302	680	45	5.0	91
<b>Group VI. Thiokol derivatives</b>								
Accelerators:								
Thionex	1	30	142	200	894	34	3.7	16
Methyl Tuads	1	20	142	256	890	35	5.5	23
Ethyl Tuads	1	15	142	238	905	33	4.1	20
Tetrone A	1	15	142	217	918	30	5.5	18
Vulcanizing Agents:								
Methyl Tuads	3	—	30	142	755	39	3.4	46
Ethyl Tuads	3	—	25	142	855	34	2.8	26
Tetrone A	3	—	25	142	738	42	4.6	7.0

TABLE III  
OZONE CRACKING—DIFFERENT ACCELERATORS

Accelerator	Static tests			Dynamic tests		
	23° C	40° C	55° C	23° C	40° C	55° C
<b>GROUP I. Guanidines</b>						
DPG	3	1	2	4	2	2
DOTG	2	1	2	4	3	2
TPG	2	1	3	4	3	4
Vulkacit 1000	2	1	1	2	1	1
<b>GROUP II. Dithiocarbamates</b>						
Methyl Zimate	3	2	3	3	2	3
Vulkacit P extra N	3	2	2	—	2	—
Ethyl Zimate	4	3	3	4	2	4
Butyl Zimate	4	3	4	4	2	3
Pipazate	3	2	3	4	1	4
Pip-pip	3	2	6	4	2	4
Vulcafor SDC	6	3	6	7	3	5
<b>GROUP III. Thiazole derivatives</b>						
Captax	4	3	4	5	3	3
Altax	4	3	4	4	3	4
Santocure	4	3	3	5	3	5
2MT	2	1	2	2	1	2
<b>GROUP IV. Condensation products</b>						
Accelerator 808	3	2	3	3	2	3
Vulkacit H	1	1	1	1	1	1
Trimene base	2	1	2	2	1	2
Trimene	2	1	2	2	1	2
Vulkacit CT	2	1	2	2	1	2
A19	2	2	2	2	1	2
<b>GROUP V. Nonclassified</b>						
NA22	2	1	2	1	1	2
Vulcafor F	3	2	3	—	2	2
<b>GROUP VI. Thiuram derivatives</b>						
Accelerators:						
Thionex	2	4	4	2	2	2
Methyl Tuads	1	4	5	2	2	4
Ethyl Tuads	4	4	5	4	3	4
Tetrone A	3	4	4	3	2	2
Vulcanizing agents:						
Methyl Tuads	6	5	6	5	4	5
Ethyl Tuads	5	4	5	4	3	4
Tetrone A	6	6	6	6	5	6

#### ANTIOXIDANTS

*Introduction.*—Shepard, Krall and Morris<sup>1</sup>, studied the influence of benzidine and concluded that ozone resistance increased with benzidine content. Somerville, Ball and Cope<sup>2</sup>, and van Rossem and Talen<sup>2</sup> found that neither Agerite Resin nor Stabilite influenced ozone resistance. More recently Thompson, Baker and Brownlow<sup>4</sup> studying neoprene vulcanizates, and Popp and Harbison<sup>5</sup> and Shaw, Ossefort and Touhey<sup>7</sup> studying GR-S, concluded that the protective power of antioxidants varies with type and that only in some cases increased ozone protection was obtained by increasing antioxidant content.

## PLATE I

Static exposure

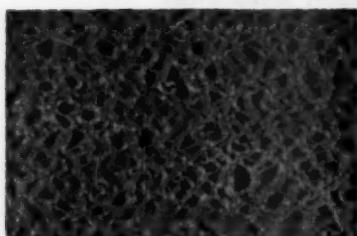


FIG. 1.—DPG.

Dynamic exposure



FIG. 5.—DPG.



FIG. 2.—Vulkacit 1000.

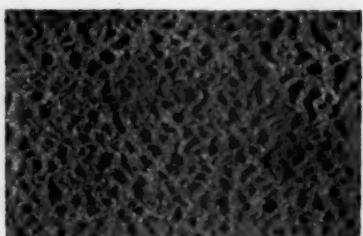


FIG. 6.—Vulkacit 1000.

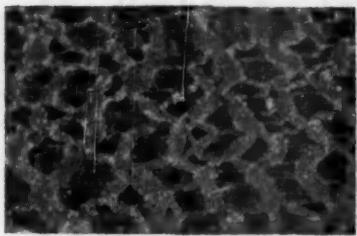


FIG. 3.—Vulkacit H.

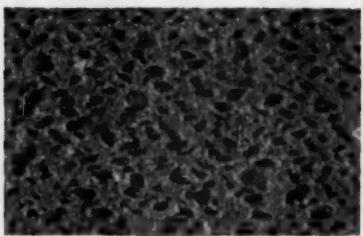


FIG. 7.—Vulkacit H.

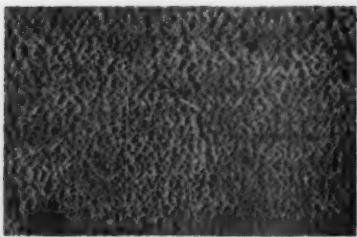


FIG. 4.—Tetrone A.

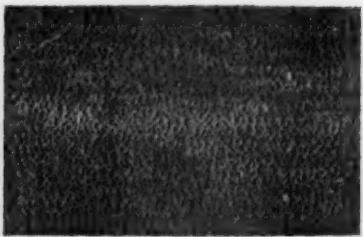


FIG. 8.—Tetrone A.

Effect of accelerators on ozone cracking (magnification 9 X).

TABLE IV  
ANTIOXIDANTS

Chemical name	Trade name
1. NN'-diphenyl ppd* (DPPD)	JZF
2. N-phenyl-N'-cyclohexyl ppd	4010
3. NN'-Di-2-naphthyl ppd	Agerite White
4. NN'-Di-2-naphthyl ppd	Nonox CI
5. Acetone-diphenylamine reaction product	BLE
6. DPPD and a diphenylamine-ketone reaction product	Flexamine
7. Phenyl-1-naphthylamine	PAN
8. Phenyl-2-naphthylamine (PBN)	Neozone D
9. Phenyl-1-naphthylamine and DPPD	Akroflex C
10. <i>p</i> ( <i>p</i> -Toluene-sulfonylamido) diphenylamine	Aranox
11. Diphenylamine-acetone condensation product	Aminox
12. PBN, DPPD and <i>p</i> -isopropoxydiphenylamine	Agerite Hipar
13. PBN, DPPD and <i>pp'</i> -dimethoxydiphenylamine	Nonox HFN
14. PBN, DPPD and <i>pp'</i> -dimethoxydiphenylamine	Thermoflex A
15. Polymerized trimethyl dihydroquinoline	Flectol H
16. Polymerized trimethyl dihydroquinoline	Agerite Resin D
17. Polymerized trimethyl dihydroquinoline	Santoflex R
18. 1,2-Dihydro 2,2,4-trimethyl 6-ethoxy quinoline	Santoflex AW
19. 1,2-Dihydro 2,2,4-trimethyl 6-phenyl quinoline and DPPD	Santoflex BX
20. 2-Mercaptobenzimidazole	MB
21. Zinc salt of mercaptobenzimidazole	MBTZ
22. 2,5-Di- <i>tert</i> -butylhydroquinone	Santovar O
23. Mixture of styrenated phenols	Styphene
24. Phenol-aldehyde-ketone reaction product	Nonox NS
25. Resorcinol-styrene condensation product	RR10
26. Butyraldehyde-aniline condensation product	Antox
27. Diarylamine-ketone-aldehyde reaction product	BXA
28. 4,4'-Dihydroxybiphenyl	DOD
29. 2,6-Di- <i>tert</i> -butyl 4-methylphenol	Ionol
30. 2,2'-Methylene bis(4-methyl-6- <i>tert</i> -butylphenol)	2246
31. 2,5-Di- <i>tert</i> -amyl hydroquinone	Santovar A
32. 4,4'-Thio-bis(6- <i>tert</i> -butyl- <i>m</i> -cresol)	Santowhite Crystals
33. Thio-bis(di- <i>sec</i> -amylphenol)	Santowhite L
34. 6- <i>tert</i> -Butyl- <i>m</i> -cresol/SCl <sub>4</sub> reaction product	Santowhite MK
35. 4,4'-Butylidene-bis(6- <i>tert</i> -butyl- <i>m</i> -cresol)	Santowhite
36. Hydroquinone monobenzyl ether	Agerite Alba
37. Styrenated phenol	Agerite Spar
38. NN'-Di- <i>sec</i> -butyl ppd	Tenamene 2
39. NN'-Di- <i>sec</i> -octyl ppd	Tenamene 30
40. NN'-Di-octyl ppd	UOP 88

\* ppd = *p*-phenylenediamine

The present investigation was made in three sections; the first was a general investigation of a number of antioxidants; the second, a special investigation of phenolic antioxidants and derivatives of *p*-phenylene diamine; and the third section, an investigation of the effect of antioxidant concentration.

The commercially available antioxidants which have been investigated are listed in Table IV, together with their chemical constitution.

*General investigation of antioxidants.*—The following base mix was used:

Crepe RMAI	100	Vulcanization temperature	142° C
Zinc oxide	5	Vulcanization time	20 mins
Stearic acid	2	Tensile strength	375 kg/cm <sup>2</sup>
Sulfur	2	Elongation at break	825 per cent
P33 carbon black	3	Shore hardness	38
Santocure	1		
Antioxidant	1.5		

TABLE V  
OZONE CRACKING—GENERAL INVESTIGATION OF ANTIOXIDANTS

Antioxidant	Static tests			Dynamic tests			Exposure test	
	23° C	40° C	55° C	23° C	40° C	55° C	Front	Back
Control	5	5	5	5	5	5	5	5
JZF	5	6	5	7	7	7	6	6
4010	6	5	5	7	7	7	7	7
Agerite White	4	5	6	5	5	5	5	4
Nonox CI	5	4	5	5	5	6	5	4
BLE	5	5	5	5	6	7	6	6
PAN	6	3	6	6	6	6	7	5
Neozone D	6	5	6	6	6	5	6	6
Akroflex C	5	3	4	6	5	6	6	5
Aminox	5	4	4	5	4	6	5	5
Agerite Hipar	6	5	6	7	7	6	6	6
Nonox HFN	6	5	4	5	4	5	5	5
Flectol H	3	1	2	5	4	5	7	7
Agerite Resin D	4	2	3	6	5	5	7	7
Santoflex BX	5	4	5	6	6	5	6	5
MB	3	3	3	4	4	4	5	4
MBTZ	3	2	2	5	4	4	6	4
Santovar O	5	4	6	7	6	5	5	5
Nonox NS	5	4	3	5	5	5	6	6
RR10	3	2	3	4	3	3	5	5
Antox	5	3	3	5	4	4	5	5
DOD	5	5	6	6	5	6	4	4

Doublewedge-shaped dumbbells were exposed under static conditions with elongations between 15 and 25 per cent; rectangular dumbbells were exposed under dynamic conditions with elongation varied between 0 and 15 per cent at a frequency of 1-1½ cps. All exposures were at 23°, 40° and 55° C to an ozone concentration of  $15 \times 10^{-8}$  ml/ml for 60 hours. The results are shown in Table V.

Some antioxidants of this series were tested again in comparison with some others at a higher ozone concentration,  $35 \times 10^{-8}$  ml/ml, for 24 hours. The results are shown in Table VI.

The results in Tables V and VI allow these antioxidants to be classified according to the ozone protection they give. To do this the grade numbers for each antioxidant are totalled for both static and dynamic tests but not for the exposure tests. The antioxidants have then been arbitrarily classified into five groups as in Table VII. Figures 9 to 18 show photographs of the cracked specimens.

TABLE VI  
OZONE CRACKING—FURTHER INVESTIGATION OF ANTIOXIDANTS

Antioxidant	Static test			Dynamic test			Exposure test	
	23° C	40° C	55° C	23° C	40° C	55° C	Front	Back
Control	6	5	6	5	4	5	4	4
JZF	5	4	4	6	4	5	5	5
4010	7	6	6	6	7	7	—	—
BLE	4	2	3	6	3	3	4	4
Flexamine	6	3	4	6	5	5	4	4
Neozone D	5	5	5	6	5	4	5	5
Akroflex C	4	3	4	6	4	4	4	4
Agerite Hipar	5	3	4	6	4	4	5	5
Santoflex R	5	5	6	6	5	5	5	5
Santoflex AW	6	6	6	7	6	6	4	4
BXA	4	4	5	6	4	4	5	3

## PLATE II

Static exposure

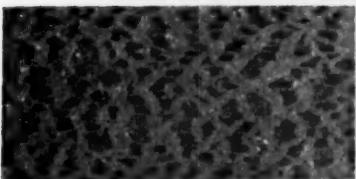


FIG. 9.—Control. No antioxidant.

Dynamic exposure

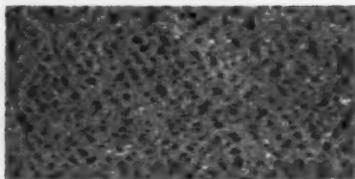


FIG. 14.—Control. No antioxidant.



FIG. 10.—1 1/2 parts 4010.



FIG. 15.—1 1/2 parts 4010.

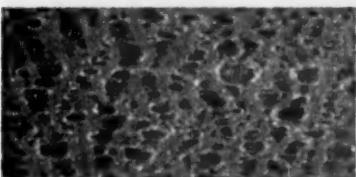


FIG. 11.—1 1/2 parts Santovar O.

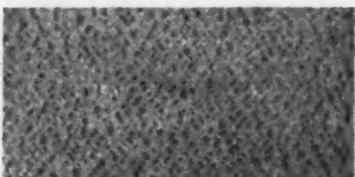


FIG. 16.—1 1/2 parts Santovar O.

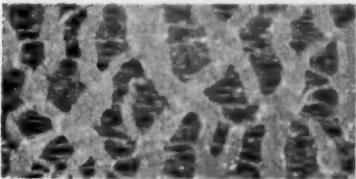


FIG. 12.—1 1/2 parts BXA.

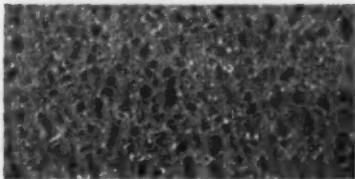


FIG. 17.—1 1/2 parts BXA.

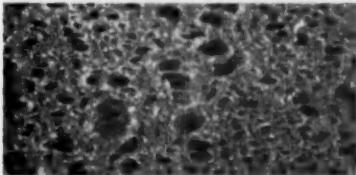


FIG. 13.—1 1/2 parts Agerite White.

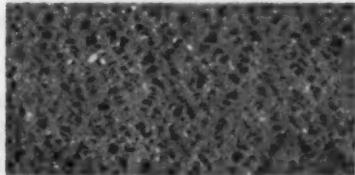


FIG. 18.—1 1/2 parts Agerite White.

Effect of antioxidants on ozone cracking (magnification 9  $\times$ ).

TABLE VII  
CLASSIFICATION OF ANTIOXIDANTS ACCORDING TO THEIR  
OZONE-PROTECTIVE POWER

Group	Sum of evaluation numbers	Antioxidants
I	42-37	JZF, 4010, Agerite Hipar, Santoflex AW
II	36-33	BLE, PAN, Neozone D, Santovar O, DOD
III	32-29	(Control), Agerite White, Nonox CI, Flexamine, Akroflex C, Aranox, Nonox HFN, Santoflex R, Santoflex BX, Styphene
IV	28-25	Aminox, Agerite Resin D, Nonox NS, BXA
V	<25	Flectol H, MB, MBTZ, RR10, Antox

*Further investigations.*—The previous sections have shown large differences in ozone-protecting power among antioxidants. Some provide good resistance, others no resistance at all and some even have a harmful effect. Because it seemed possible that ozone protection might be related to chemical structure of the antioxidants, further experiments were carried out.

TABLE VIII  
OZONE CRACKING—PHENOLIC ANTIOXIDANTS

Antioxidant	Static test			Dynamic test		
	23° C	40° C	55° C	23° C	40° C	55° C
Control	4	6	5	4	6	5
2246	4	5	5	4	6	5
Santovar A	3	4	5	3	5	4
Santovar O	3	5	6	4	6	5
Santowhite Crystals	2	4	4	2	5	4
Santowhite L	6	6	6	6	6	6
Santowhite MK	3	6	6	4	5	5
Santowhite Powder	2	5	5	2	4	3
Agerite Alba	1	3	3	4	5	4
Agerite Spar	5	6	5	5	4	4
Ionol	4	5	5	1	3	3
RR10	3	2	3	4	3	3
DOD	5	5	6	6	5	6
4010	7	6	5	6	7	7
Santoflex AW	6	6	7	6	7	7

*Phenolic antioxidants.*—For this work the base mix and testing procedure already described were used except that the ozone concentration was  $25 \times 10^{-8}$  ml/ml and the time of exposure was 30 hours. The ozone-cracking results are given in Table VIII. The nonphenolic antioxidants 4010 and Santoflex AW were included so that all five groups in Table VII should be represented. Figures 19 to 26 show photographs of the cracked specimens.

TABLE IX  
CLASSIFICATION OF PHENOLIC ANTIOXIDANTS

Group	Sum of evaluation numbers	Antioxidants
I	42-37	4010, Santoflex AW
II	36-33	DOD, Santowhite L
III	32-29	(Control), Santovar O, 2246, Santowhite MK, Agerite Spar
IV	28-25	RR10, Ionol, Santovar A, Santowhite Crystals,
V	<25	Santowhite Powder, Agerite Alba

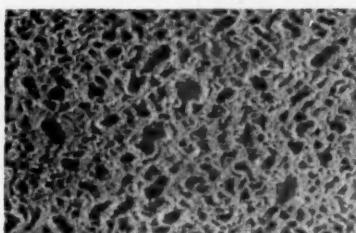
PLATE III  
Static exposure

FIG. 19.—Control. No antioxidant.

PLATE III

Dynamic exposure

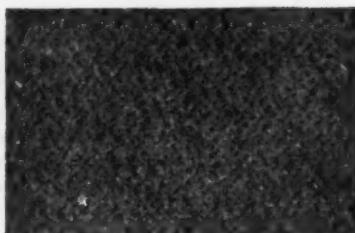


FIG. 23.—Control. No antioxidant.

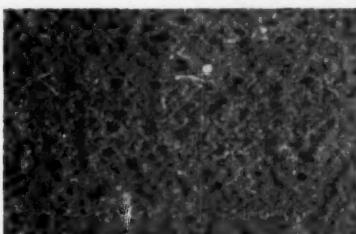


FIG. 20.—1½ parts 2246.

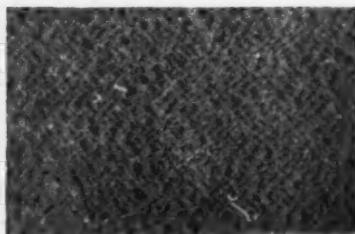


FIG. 24.—1½ parts 2246.

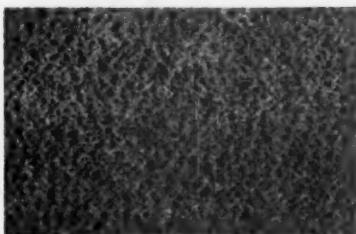


FIG. 21.—1½ parts Santowhite L.



FIG. 25.—1½ parts Santowhite L.

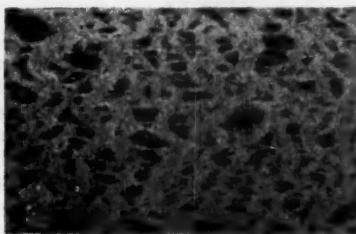


FIG. 22.—1½ parts Santowhite Powder.

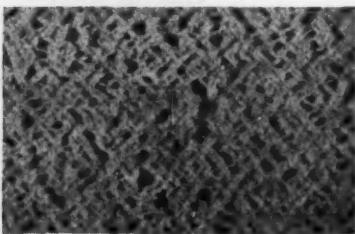


FIG. 26.—1½ parts Santowhite Powder.

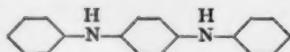
Effect of phenolic antioxidants on ozone cracking (magnification 9 X).

Table IX shows the antioxidants in Table VIII classified in groups in the same way as those in Table VII.

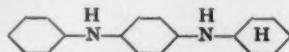
There are no phenolic antioxidants in Group I and only two in Group II; the others are found in Groups III and V. This suggests that phenolic antioxidants give only moderate protection to natural rubber vulcanizates.

*p*-Phenylenediamine derivatives.—The classification of antioxidants in Table VII shows differences among the protective properties of the various *p*-phenylenediamine derivatives and suggests that differences in protective power depend on the substituent groups attached to the nitrogen atoms. The following *p*-phenylenediamine derivatives have now been investigated.

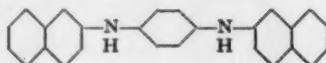
(1) NN'-Diphenyl ppd



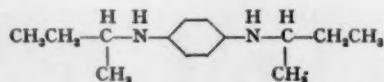
(2) N-Phenyl-N'-cyclohexyl ppd



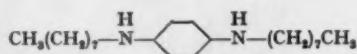
(3) NN'-Di-2-naphthyl ppd



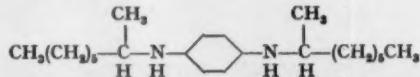
(4) NN'-Di-*sec*-butyl ppd



(5) NN'-Di-octyl ppd



(6) NN'-Di-*sec*-octyl ppd



Kahn<sup>6</sup> made a similar investigation in GR-S and concluded that the best ozone protection was obtained when the number of carbon atoms in the substituent group was between 6 and 10. Shaw, Ossefort and Touhey<sup>7</sup> found that good protection was given by NN'-dioctyl ppd and they put forward the theory that this protection depends on the rate of migration of the antiozonant to the surface of the rubber and on the rate of loss of the antiozonant by evaporation at the surface. Extending this reasoning it seems possible that ozone resistance might be improved by increasing the rate of migration of the antiozonant; this might be done by adding a small amount of a paraffin wax which would act as a "carrier" for the antiozonant.

TABLE X  
OZONE CRACKING—*p*-PHENYL DIAMINE DERIVATIVES

Antioxidant	Paraffin	Static test, Time in hours										Dynamic test, Time in hours										
		30	54	78	102	118	142	183	207	237	267	30	54	78	102	118	142	183	207	237		
NN'-Di-2-naphthyl ppd	—	4	3	2	—	1	—	1	—	—	—	—	4	2	2	1	—	1	1	—	—	
NN'-Diphenyl ppd	—	5	4	4	4	—	3	—	2	1	—	—	5	4	3	3	—	3	—	1	—	
N-Phenyl-N'-cyclohexyl ppd	—	6	4	3	—	2	—	1	—	—	—	—	6	5	4	—	3	—	2	—	—	
NN'-Di- <i>sec</i> -butyl ppd	—	5	5	4	4	—	3	—	1	—	—	—	6	5	5	3	—	2	—	1	—	
NN'-Di- <i>sec</i> -octyl ppd	—	7	7	7	7	—	7	—	7	7	7	7	7	7	6	5	—	4	—	2	2	
NN'-Di-octyl ppd	—	7	7	6	6	6	—	6	—	5	3	3	3	2	6	6	5	4	—	3	—	
Santoflex AW	—	7	6	6	5	—	5	—	1	—	—	—	4	3	2	—	1	—	1	—	—	
Control	—	4	4	3	—	2	—	1	—	—	—	—	—	—	—	—	—	—	—	—	—	
NN'-Di-2-naphthyl ppd	2 d	1	1	1	—	1	—	1	—	—	—	—	—	—	—	—	—	—	—	—	—	
NN'-Diphenyl ppd	2 d	5	4	4	4	—	3	—	2	1	—	—	—	4	3	2	2	—	2	—	1	1
N-Phenyl-N'-cyclohexyl ppd	2 d	7	7	6	5	—	5	—	4	3	3	2	2	5	4	3	3	—	3	—	1	1
NN'-Di- <i>sec</i> -butyl ppd	2 d	5	4	4	4	—	3	—	1	—	—	—	6	4	4	3	—	2	—	1	—	—
NN'-Di- <i>sec</i> -octyl ppd	2 d	7	7	7	7	—	7	—	7	7	7	7	7	7	6	5	5	4	—	2	1	—
NN'-Di-octyl ppd	2 d	6	6	5	5	—	4	2	1	1	—	—	—	6	5	5	4	—	2	—	1	1
Santoflex AW	2 d	7	6	6	5	—	5	—	4	3	3	2	2	6	4	3	3	—	2	—	1	1
Control	2 d	1	1	1	—	1	—	1	—	—	—	—	—	1	1	1	—	—	—	—	—	—

To test this theory for natural rubber experiments were made with and without small amounts of paraffin wax. All specimens were exposed to an ozone concentration of  $25 \times 10^{-8}$  ml/ml under both static and dynamic conditions. The results are given in Table X.

Table X shows that in vulcanizates without paraffin wax NN'-di-sec-octyl ppd gives the best results; it prevents crack formation even after 407 hours static exposure. NN'-Di-octyl ppd and 2,2,4-trimethyl-1,2-dihydro-6-ethoxy-quinoline, though not as good as di-sec-octyl ppd, give much better protection

TABLE XI  
OZONE CRACKING—EFFECT OF ANTIOXIDANT LOADING

Temperature Concentration	Static test						Dynamic test								
	23° C		40° C		55° C		23° C		40° C		55° C				
	1½	3	6	1½	3	6	1½	3	6	1½	3	6	1½	3	6
Control	4		6		6		4		5		5		5		5
JZF	6	5	3	6	5	4	6	6	6	5	6	6	7	7	6
4010	7	7	5	6	7	6	7	7	7	7	7	7	7	7	7
Agerite White	4	5	6	7	6	7	6	6	6	5	6	5	5	5	6
Nonox X1	4	4	4	6	6	6	6	6	5	5	5	5	5	5	5
BLE	5	4	4	5	5	5	5	7	6	5	5	6	6	6	5
Flexamine	5	5	5	6	5	5	5	6	5	6	5	6	6	6	6
PAN	4	4	4	6	6	6	6	6	4	4	4	5	5	4	5
Neozone D	5	6	6	6	6	6	6	6	5	5	4	5	6	5	4
Akroflex C	4	3	4	6	4	6	5	6	5	6	5	5	5	5	5
Aranox	4	4	4	6	6	6	6	6	3	4	5	5	5	5	5
Aminox	2	3	2	2	4	2	5	5	5	4	4	4	4	4	4
Agerite Hipar	5	6	6	6	7	7	6	6	7	6	5	5	6	5	5
Nonox HFN	6	6	6	6	7	7	6	6	5	5	4	6	6	5	6
Thermoflex A	3	5	5	7	7	7	6	6	7	5	5	4	6	7	5
Fleetol H	1	1	7	3	2	4	2	2	3	4	3	3	4	4	4
Santoflex R	4	4	3	5	5	5	3	5	6	5	6	6	5	5	6
Santoflex AW	5	6	6	7	7	6	6	7	7	6	7	7	7	7	7
Santoflex BX	4	6	6	6	6	7	6	6	7	5	6	6	7	6	7
MB	2	2	1	4	4	4	2	1	2	4	4	4	4	4	4
MBTZ	2	1	1	5	4	4	4	2	1	3	4	1	4	3	1
Santovar O	3	4	4	5	5	5	6	6	5	5	5	5	5	5	5
Styphene	5	5	5	7	6	6	6	6	4	5	3	6	6	6	5
Nonox NS	2	1	1	3	4	4	2	3	3	4	4	4	5	4	4
RR10	2	2	2	3	3	3	4	3	3	5	5	5	4	5	3
Antox	2	2	2	3	3	3	4	3	3	5	5	4	5	5	6
BXA	2	1	2	3	3	2	3	3	3	3	4	4	4	4	5
DOD	5	5	5	6	6	6	6	5	5	5	4	6	6	6	5

than the antioxidants which have previously been used. The cracking of vulcanizates containing NN'-di-phenyl ppd, N-phenyl-N'-cyclohexyl ppd or NN'-di-2-naphthyl ppd is about the same as the control.

The addition of  $\frac{1}{2}$  part paraffin wax improves the protection given by N-phenyl-N'-cyclohexyl ppd only; this is then as good as 2,2,4-trimethyl-1,2-dihydro-6-ethoxy quinoline.

*Influence of antioxidant concentration.*—The experiments described in this section were made before the ppd derivatives of the preceding section became available.

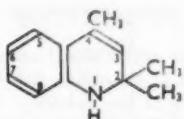
To show whether increased antioxidant loading would give better ozone protection,  $1\frac{1}{2}$ , 3 or 6 parts of antioxidant per 100 of rubber were added to the base mix used previously. Doublewedge-shaped dumbbells were exposed

statically for 30 hours to an ozone concentration of  $25 \times 10^{-8}$  ml/ml. Ozone cracking results are given in Table XI.

Table XI shows that only with Santoflex BX does ozone protection improve with loading. In most cases changing the loading has little effect though with RR10 and MBTZ protection becomes less.

*Importance of chemical structure.*—Most phenolic antioxidants have no effect, either good or bad, on ozone cracking.

Of the quinoline derivatives, 2,2,4-trimethyl-1,2-dihydroquinoline derivatives such as Flectol H, Agerite Resin D and Santoflex R have no effect, or make cracking worse. Protection against ozone is given when the 6-position is substituted.



Santoflex BX is the 6-phenyl derivative and Santoflex AW is the 6-ethoxy derivative.

Imidazole compounds such as MB or MBTZ make cracking worse.

The aromatic amines can be divided in two groups. In the first are the phenyl naphthylamines, PAN and PBN, which give only moderate protection; the second group contains the ppd derivatives and shows considerable variation in protective properties. The diphenyl and dinaphthyl derivatives have no effect but the phenyl-cyclohexyl and dioctyl derivatives give good protection. Di-*sec*-octyl ppd gives the best protection in natural rubber, but in GR-S di-octyl ppd is best. Ppd derivatives have to be handled with care because they tend to irritate the skin.

### SUMMARY

An investigation of the ozone protection given to natural rubber vulcanizates by different accelerators and antioxidants has shown that, of the accelerators investigated, the thiuram derivatives appear to be the best antioxidants, when they are used as vulcanizing agents; of the large number of antioxidants examined. NN'-di-*sec*-octyl *p*-phenylene diamine appears to be the best antiozonant. Vulcanizates containing this material showed no cracks after being exposed for 400 hours to an ozone concentration of  $25 \times 10^{-8}$  ml/ml under static conditions; it was far superior to all other materials examined.

### ACKNOWLEDGMENTS

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# ON THE RELATION BETWEEN INDENTATION HARDNESS AND YOUNG'S MODULUS \*

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## INTRODUCTION

The stiffness of rubber units under small compressive or tensile strains may be calculated by means of an appropriate function of the dimensions and a value for the Young's modulus of the rubber. It is desirable therefore to be able to determine the value of Young's modulus for vulcanized rubbers by a less laborious method than the examination of tall thin columns under very small deflections. The measurement of indentation hardness should be suitable for this purpose, and the British Standard method described in B.S.903 (1950 and 1957) is, in fact, stated to provide a measure of Young's modulus also. The relation between the British Standard and International rubber hardness and Young's modulus is discussed below.

As the B.S. & I.R.H. scale and the Shore durometer hardness scale are virtually equivalent over the central regions, the Shore instrument should also provide a means of determining Young's modulus. The relation between Shore hardness and Young's modulus is discussed in a later section.

## THE RELATION BETWEEN BRITISH STANDARD AND INTERNATIONAL RUBBER HARDNESS AND YOUNG'S MODULUS

*Theoretical treatment.*—The B.S. hardness test<sup>1</sup> consists essentially of the measurement of the increase in depth of penetration of a rigid spherical indentor into a flat pad of rubber when the applied load is increased from 30 to 570 g.

The British Standard and International rubber hardness is not quoted directly as the increase in indentation but as a numerical value denoted "B.S. & I.R.H. degrees" related to this in a complex manner<sup>1,2,3</sup>. The form of the relation is not relevant to the present discussion; it may be noted merely that the hardness scale has been chosen so that values of 0° and 100° B.S. & I.R.H. correspond to infinitely large and zero values of the increase in indentation, respectively, and the scale conforms approximately with the Shore hardness scale over the central region. Corresponding values of B.S. & I.R.H. degrees and the increase in indentation  $d_1$  are represented graphically in Figure 1.

Provided the indentation is sufficiently small and the rubber sufficiently reversible and isotropic, the relation between the total amount of indentation  $d$  and the value of Young's modulus  $E$  for the rubber is given by classical elasticity theory<sup>4</sup> in the form:

$$d^{\frac{1}{2}} = F/1.78Er^{\frac{1}{2}} \quad (1)$$

where  $F$  is the load applied to the indentor, and  $r$  is the radius of the spherical end.

\* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 34, pages 46-57 (1958). (ICCR Class No. 63425.)

When the appropriate values of initial and final load  $F$  and indentor radius  $r$  (0.122 cm) are used, the following relation is obtained from Equation (1) for Young's modulus  $E$  in terms of the increase in indentation  $d_1$ :

$$E = 0.731/d_1^{1/2} \quad (2)$$

where  $E$  and  $d_1$  are measured in kg/cm<sup>2</sup> and cm, respectively.

The relation between Young's modulus  $E$  and the British Standard and International rubber hardness, corresponding to the relation given in Equation (2) between  $E$  and  $d_1$ , is represented graphically by the full curve in Figure 2.

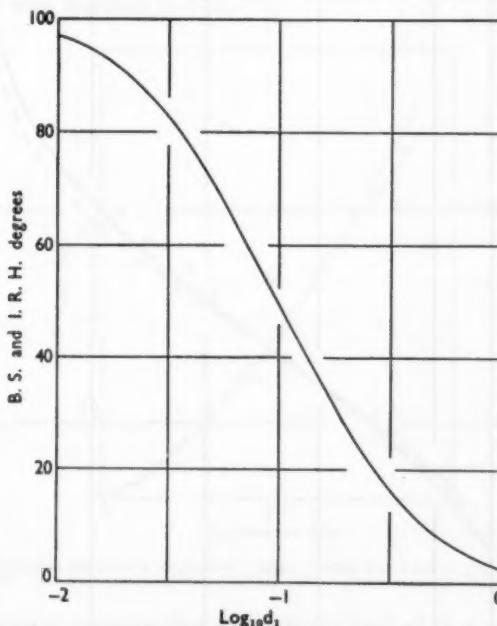


FIG. 1.—Relation between the British Standard and International rubber hardness and the increase in indentation  $d_1$  under standard loading conditions, using 0.244 cm diameter ball.

*Relation given in B.S.903 (1950).*—The derivation of a relation not greatly dissimilar to that obtained in the preceding section is outlined in B.S.903 (1950). In place of the relation given in Equation (1) above, obtained from classical elasticity theory, an empirical relation is used which was obtained by Scott<sup>5,6</sup> from a study of the indentation behavior of various vulcanizates, using two indentors of different radii. The relation takes the form:

$$d^{1.35} = F/1.91Er^{0.66} \quad (3)$$

where the symbols have the same significance as before. The three numerical constants were determined experimentally, in contrast to those used in Equation (1). When the appropriate values of initial and final load  $F$  and indentor

radius  $r$  are used, the following relation is obtained for Young's modulus  $E$  in terms of the increase in indentation  $d_1$ :

$$E = 1.00/d_1^{1.35} \quad (4)$$

The corresponding relation between  $E$  and the British Standard and International rubber hardness is represented graphically by the broken curve in Figure 2. An equivalent relation between  $E$  and the indentation hardness in B.S. degrees is given on page 114 of B.S.903 (1950).

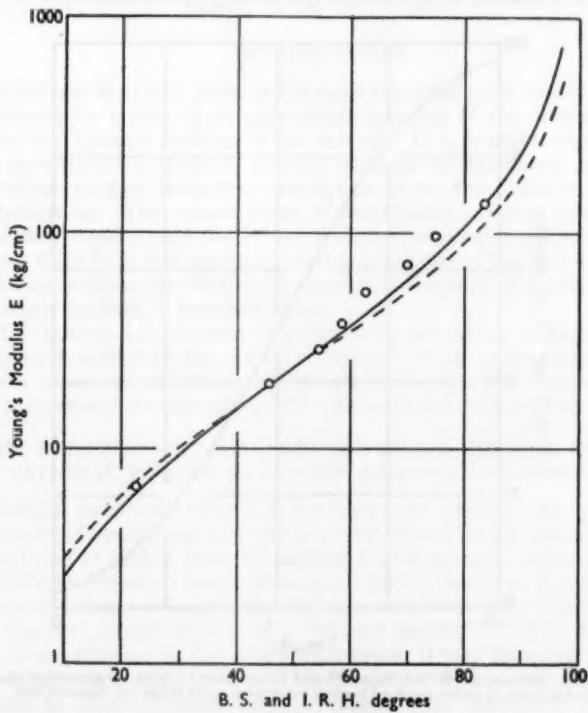


FIG. 2.—Relation between Young's modulus  $E$  and the British Standard and International rubber hardness. Full curve: theoretical relation. Broken curve: empirical relation obtained from B.S.903 (1950). Open circles: experimental measurements.

It is seen from Figure 2 that the empirically obtained relationship of Equation (4) is in fairly close accord with that obtained theoretically, given in Equation (2). Significant departures occur, however, the theoretical curve predicting greater values for Young's modulus than the empirical relationship at hardnesses exceeding about 60°, and smaller values at hardnesses of less than about 30°. These differences presumably arise from differences in the two relations for the indentation of a flat pad by a rigid spherical indentor, Equations (1) and (3). It was therefore considered desirable to examine the load-indentation relationship experimentally.

*Experimental examination of load-indentation relationship.*—Measurements were made of the indentations caused by applying various loads to a spherical indenter, similar to that specified in the B.S. hardness test. The indenter was attached to the lower end of the operating column of a dial gage, the main spring of which had been removed, leaving an initial load of 35 g acting on the indenter. The assembly was rigidly supported above a flat baseplate on which a rubber testpiece rested, the indentation therefore being measured with respect to the baseplate.

The testpiece comprised two pads of a soft natural rubber vulcanizate, each 0.5 cm thick and of square section of about 7 cm length of side, placed together to give an effective thickness of 1 cm.

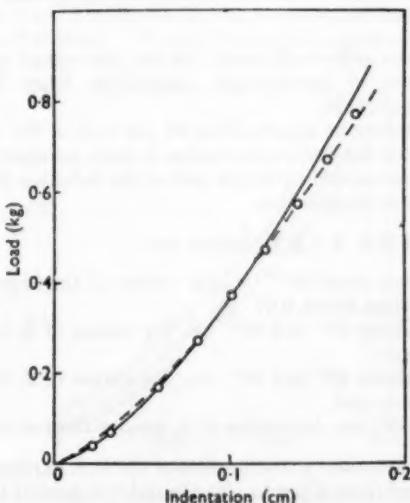


FIG. 3.—Load-indentation relation for a spherical indenter pressed into a rubber pad. Full curve: theoretical relation. Broken curve: empirical relation. Open circles: experimental measurements.

The indentation corresponding to the initial load of 35 g was determined from the decrease in the apparent thickness of the test-piece when the indenter foot was substituted for a flat cylindrical plate of 1 cm diameter. Additional loads were then applied by adding weights to the operating column of the dial gage. The measurements of total load and total indentation are presented graphically in Figure 3, the experimental points being denoted by open circles. No significant difference was observed between the indentations attained during the load-increasing and load-decreasing measurements.

The full curve of Figure 3 is of the form predicted by theory and given in Equation (1), with the value of  $E$  chosen to give agreement with the experimental measurements at small indentations. The value so obtained was 18.6  $\text{kg}/\text{cm}^2$ , in good agreement with that determined directly from small compressions of tall cylinders, i.e., 20.0  $\text{kg}/\text{cm}^2$ . The broken curve of Figure 3 is of the empirical form given in Equation (3), with the value of  $E$  chosen to give the best agreement with the experimental measurements. The value so obtained was 17.0  $\text{kg}/\text{cm}^2$ , in fair accord with that determined directly.

It is seen in Figure 3 that the load-indentation relationship is accurately described by the theoretical relation given in Equation (1) for indentations of up to about 50 per cent of the diameter of the spherical indentor, in general accord with the observations of Larrick<sup>7</sup>. Thereafter, departures become increasingly serious. The empirical relation, on the other hand, appears to describe large indentations exceeding about 30 per cent of the diameter of the indentor with considerable success, but for indentations below this it is seen to predict smaller indentations than are observed, the differences being relatively large. It has been reported that it becomes inapplicable for indentations of more than 80 per cent of the indentor diameter also<sup>8</sup>.

One may distinguish therefore four sections of the British Standard and International rubber hardness scale, corresponding to four ranges of indentation, namely,

- (i) indentations sufficiently small for the theoretical relation to apply;
- (ii) indentations of intermediate magnitude when both relations are equally applicable;
- (iii) large indentations approaching 80 per cent of the diameter of the indentor when the empirical relation is more accurate, and
- (iv) indentations exceeding 80 per cent of the indentor diameter, when both relations are inapplicable.

The equivalent B.S. & I.R.H. ranges are:

- (i) greater than about  $60^\circ$ , i.e., for values of the increase in indentation  $d_1$  or less than about 0.07 cm;
- (ii) between about  $38^\circ$  and  $60^\circ$ , i.e., for values of  $d_1$  between about 0.14 and 0.07 cm;
- (iii) between about  $33^\circ$  and  $38^\circ$ ; i.e., for values of  $d_1$  between about 0.17 and 0.14 cm, and
- (iv) less than  $33^\circ$ , i.e., for values of  $d_1$  greater than about 0.17 cm.

Blackwell<sup>9</sup> has proposed a modification of the B.S. hardness test in which the total load is reduced from 570 g to 100 g in order to permit the measurement of hardness below  $30^\circ$ . It may be inferred that the corresponding indentations for hardness values down to  $10^\circ$  will be sufficiently low for the theoretical load-indentation relation to be applicable accurately. If reduced major loads are used for determining hardness values of less than  $35^\circ$  to  $40^\circ$  B.S. & I.R.H., the theoretical relation will be applicable throughout the entire useful range, more accurately than the empirical relation of Equation (3) in important regions, and about equally so elsewhere.

*Experimental examination of load-indentation relationship, when a dial gage foot is employed as a reference plane.*—In the preceding section experiments were described in which the load-indentation relationship for a spherical indentor was examined, the indentation being measured with respect to a fixed reference plane, namely the baseplate on which the rubber testpiece rested. Under these circumstances the theoretically-derived relation appeared to predict the load-indentation behavior satisfactorily over the major part of the normal range of indentation, whereas the empirical relation proved inapplicable at small indentations.

However, the method of measurement specified in B.S.903 (1950 and 1957) for measurements on standard testpieces, and that used by Scott<sup>5,6</sup> in establishing the empirical relation given in Equation (3), differs in one respect from

that described in the preceding section. The dial gage is supported by a foot which rests on the surface of the testpiece and exerts a considerable pressure upon it. The indenter and operating column of the dial gage pass through a central hole in the foot to bear on the surface of the rubber testpiece. The indentation is therefore measured with respect to the lower surface of the foot.

In order to examine whether this change in the method of measurement affects the conclusions of the previous section, a further series of experiments was carried out. The testpiece used consisted of a block of a soft natural rubber vulcanizate, 1.8 cm thick and of square section of about 5 cm length of side.

The first experiment was designed to establish the validity of the theoretical relation at low indentations more precisely than before, and a dial gage was not employed. The indenter was suspended from a soft helical steel spring, having a stiffness of about 1 g/cm, so that its lowest point lay slightly above the upper surface of the testpiece. Weights were then added to the indenter, the

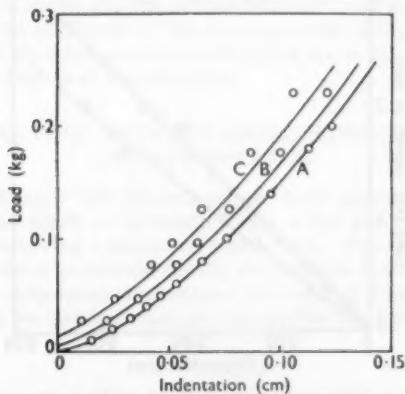


FIG. 4.—Load-indentation relation for a spherical indenter pressed into a rubber pad. A: indentation measured with respect to base-plate. B: indentation measured with respect to dial gage foot, the load acting on the foot being 0.85 kg. C: indentation measured similarly, the load acting on the foot being 2.85 kg. Full curves: theoretical relation, displaced laterally by amounts obtained from measurements given in Figure 5, at appropriate foot loads.

corresponding indentations being observed by means of a microscope having an eyepiece scale. The measurements of load and indentation are denoted by the open circles in Figure 4, Curve A. The full curve is of the form predicted by theory and given in Equation (1); it is seen to describe the experimental results satisfactorily, in agreement with the earlier measurements reported in the preceding section.

A series of measurements was then carried out with the indenter attached to the operating column of the dial gage, which was supported by an annular foot of the dimensions specified in B.S.903 (1950 and 1957). By pressing the assembly against a flat glass plate, the dial gage reading was obtained when the indenter lay in the plane of the lower surface of the foot. The load-indentation relationship for the rubber testpiece was then obtained by adding weights to the operating column of the dial gage and observing, by means of the dial gage, the movement of the indenter with respect to the foot. The measurements of load and indentation are denoted by the open circles in Figure 4, Curves

*B* and *C*, for two different loads acting on the annular foot, 0.85 and 2.85 kg, respectively. The first of these values corresponds to the foot pressure specified in B.S.903 (1950 and 1957).

It is seen that the indentations are reduced on increasing the pressure applied to the foot. Moreover there is a marked indication that a negative indentation would be observed at low loads. It seems probable that the pressure applied to the foot causes the rubber to bulge upwards in the central hole. A negative indentation would then be registered for sufficiently small loads applied to the indenter, since it would be raised above the plane of the lower surface of the foot.

In order to examine the magnitude of this effect, measurements were made by means of a dial gage of the vertical movement of an annular foot under increasing loads, and also of the rubber surface under the central hole. The

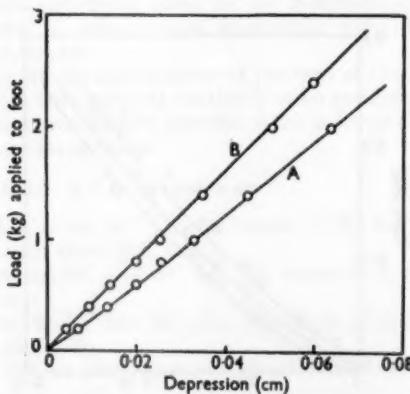


FIG. 5.—Depression of dial gage foot (Curve *A*) and of rubber surface under central hole in foot (Curve *B*) at various loads applied to the foot.

depression of the foot is shown in Curve *A*, and of the rubber surface within the central hole in Curve *B*, of Figure 5. It is seen that the foot is depressed more than the rubber surface, the difference being a measure of the upwards bulging of the rubber in the central hole as the foot pressure increases.

The two values of the upwards bulge of the rubber surface, corresponding to the two loads applied to the dial gage foot in determining Curves *B* and *C* of Figure 4, may be obtained from the differences between the experimental curves of Figure 5 at the appropriate loads. When the values obtained are subtracted from Curve *A* of Figure 4, the full Curves *B* and *C* are obtained. It is seen that they are in good agreement with the experimental measurements at low loads, although at large loads the observed indentations are somewhat smaller than those predicted, presumably due to the restricting influence of the foot. Soden<sup>10</sup> has reported small increases in the apparent hardness of soft vulcanizates when measured with a foot-type instrument. However, the theoretical relation is seen to describe the load-indentation behavior with fair success when the indentation is measured with respect to the dial gage foot, and the relation given in Equation (2) between the increase in indentation under

standard loading conditions and the value of Young's modulus will therefore be approximately applicable to such measurement also.

It seems probable that the empirical load-indentation relation given in Equation (3) was originally obtained by attempting to fit experimental measurements such as those shown in Curve *B* of Figure 4 with a smooth curve passing through the origin. The present measurements show that when no load is applied to the indentor there is a negative indentation, due to an upwards bulging of the rubber under the pressure exerted by the foot.

*Experimental measurements of indentation hardness and Young's modulus.*—Measurements were made of the British Standard and International rubber hardness of six natural rubber vulcanizates containing various quantities of lampblack, and of two which contained no carbon black. The hardness of the softest vulcanize (22.5°) was determined using Blackwell's modified loading conditions. Load-deflection relations were also obtained for small compressions of tall thin cylinders prepared from the same recipes. Corresponding values of Young's modulus and the British Standard and International rubber hardness are plotted in Figure 2, the measurements being denoted by open circles. It is seen that the experimental points are in fairly good agreement with the theoretical curve of Equation (2).

#### THE RELATION BETWEEN SHORE HARDNESS AND YOUNG'S MODULUS

*Theoretical treatment.*—The Shore hardness test<sup>11</sup> consists essentially of the measurement of the depth of indentation into a flat pad of rubber of a rigid cylindrical indentor having a truncated conical end. Provided the indentation is small and the rubber reversibly elastic, the relation between the amount of indentation *d* for a cylindrical indentor and the value of Young's modulus *E* for the rubber is given by classical elasticity theory<sup>12</sup> in the form

$$d = F/2.67Er$$

where *F* is the load applied and *r* is the radius of the indentor. The Shore indentor tapers at the end from a cylindrical shaft having a radius of 0.0635 cm to a circular end face having a radius of 0.0395 cm over a distance of about 0.077 cm. We may assume as a first approximation that the indentor is equivalent to a cylinder having a radius equal to the mean radius of the conical end, namely 0.0515 cm, and this value for *r* is used in the following calculations.

The indentor is attached to a spring in the instrument and protrudes by an amount 0.254 cm. When the instrument is pressed against the rubber so that the base is in contact with the surface of the rubber, the amount by which the spring is compressed *c* and the indentation of the rubber *d* together equal the original protruding length of the indentor, i.e.,

$$c + d = 0.254 \text{ cm} \quad (6)$$

The spring compression *c* is indicated on a linear scale, one degree being equivalent to  $2.54 \cdot 10^{-3}$ . From Equation (6), therefore, the amount of indentation *d* at a scale reading of *s* degrees is given by

$$d(\text{cm}) = 0.254 - 2.54 \cdot 10^{-3}s \quad (7)$$

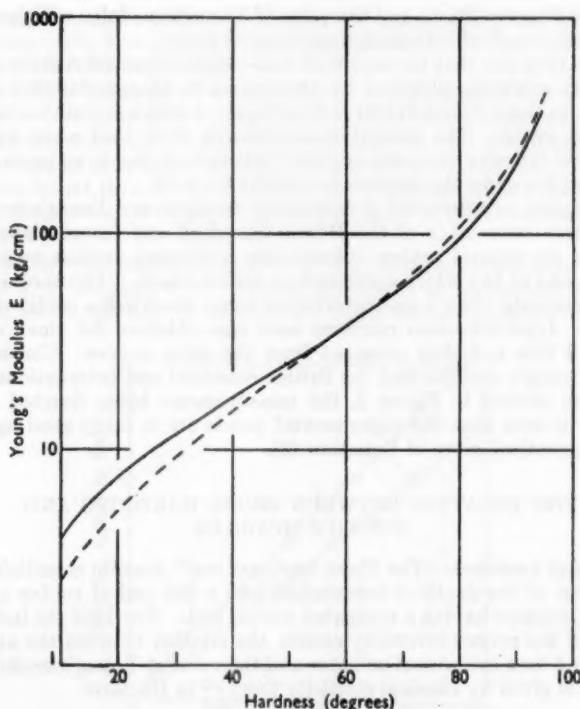


FIG. 6.—Relation between Young's modulus and Shore hardness. Full curve: approximate theoretical relation. Broken curve: theoretical relation between Young's modulus and the British Standard and International rubber hardness.

The force acting on the indentor when the spring is compressed by  $s$  scale degrees is given by<sup>11</sup>

$$F(\text{kg}) = 0.056 + 7.66 \cdot 10^{-3}s \quad (8)$$

Substituting in Equation (5) for  $d$  from Equation (7), and for  $F$  from Equation (8), and transposing, we obtain

$$E(\text{kg/cm}^2) = \frac{56 + 7.66s}{2.67r(254 - 2.54s)} \quad (9)$$

On introducing into Equation (9) the appropriate value for the mean radius  $r$  of the end section of the indentor, the full curve of Figure 6 is obtained for the relation between Young's modulus  $E$  and Shore hardness  $s$ . For comparison the relation derived theoretically between Young's modulus and the British Standard and International rubber hardness is represented by the broken curve of Figure 6. It is seen that good agreement obtains for values of hardness exceeding about 40°, providing support for the assumptions made in deriving

the two relations and also providing confirmation of the approximate equivalence of the British Standard and International rubber hardness and Shore hardness scales over the major part of the hardness range.

### GENERAL CONCLUSIONS

*General conclusions.*—The following conclusions are obtained:

(1) The load-indentation relationship for a rigid spherical indentor pressed into a flat rubber pad is amenable to theoretical analysis for sufficiently small indentations.

(2) The relation between load and indentation, when the latter is measured with respect to a dial gage foot pressing on the surface of the rubber testpiece, is also found to be that predicted theoretically. The origin is displaced by an amount corresponding to the upwards bulging of the rubber into the central hole in the foot.

(3) The empirical relation between load and indentation obtained by Scott<sup>5,6</sup> is inapplicable at small indentations.

(4) The theoretical relation between the British Standard and International rubber hardness and Young's modulus is as accurately applicable as the empirically-obtained relation given in B.S.903 (1950) for rubbers of hardness between about 40° and 60° and more so for rubbers of hardness exceeding about 60°. The numerical constants, moreover, are not subject to experimental uncertainty.

(5) If reduced major loads are stipulated for rubbers of hardness less than about 35 to 40 B.S. & I.R.H. degrees, the theoretical relation should be applicable throughout the entire useful range.

(6) The relation between Shore hardness and Young's modulus is amenable to an approximate theoretical analysis. The approximate equivalence of the British Standard and International rubber hardness and Shore hardness scales is confirmed.

### SUMMARY

A relation between British Standard and International rubber hardness and Young's modulus is derived from classical elasticity theory, and compared with the empirical relation given in B.S.903:1950. An experimental examination of the load-indentation relationship for a rigid sphere pressed into a flat rubber pad is described; it indicates that the theoretical relation is more appropriate than the empirical one for small indentations, corresponding to hardnesses exceeding about 60° B.S. & I.R.H., and equally valid for hardnesses between about 40° and 60°. Moreover, the numerical constants are not subject to experimental uncertainty. If reduced major loads are stipulated for determining the hardness of rubbers of less than 35° to 40° B.S. & I.R.H., the theoretical relation should apply over the entire useful range.

An approximate relation between Shore hardness and Young's modulus is derived similarly. The approximate equivalence of the British Standard and International rubber hardness and Shore hardness scales over the major part of the hardness range is confirmed.

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# SPEED OF MIXING RUBBER AS A FACTOR IN PROCESSING \*

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## INTRODUCTION

The mixing of ingredients is one of the fundamental steps in the preparation of rubber compounds and any increase in the speed of this process is of great significance to the rubber industry. The following methods are being put into practice for speeding up this process:

1. The use of mechanical weighing and loading of the materials used in the mixing process.
2. Increasing the speed of rotation of the mixing rotors and applying higher pressures to the mixing chamber.

In foreign countries the rotor speed is increased from 20 to 30, 40, 50 and in some cases 60 rpm. The pressure on the mixing chamber is increased from 0.5-1 to 4 or 5 and sometimes 10 kg/cm<sup>2</sup>. The most useful type of foreign construction is a two (odd) speed mixer in which mixing time is considerably shortened.

There is very little literature concerning the process of mixing. What there is does not give the experimental materials or a complete presentation of the mechanism of mixing of rubber with the fillers. Therefore, it may be useful to give the fundamental results of our work which was done in the NIIShP laboratory in 1954-1955.

This work was devoted to a study of some characteristics of mixing of SK (synthetic rubber) as a function of mixing speed, the influence of technological factors on dispersion of ingredients and the effect of higher mixing temperature on the properties of compounds of synthetic rubbers.

## METHOD

Most of the experiments on mixture preparation were done in a laboratory mixer having the following characteristics:

Capacity of mixing chamber, 2 liters

Speed of rotation of rotors, rpm, in the following combinations:

Front rotor	27	33.5	42	53	67	84
Rear rotor	32	40	50	63	80	100

Capacity of load in mixer, 1.5 kg

The mixing chamber was equipped with a jacket for cooling with water or heating with steam.

\* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for RUBBER CHEMISTRY AND TECHNOLOGY from *Kauchuk i Resina*, 1957, No. 4, pages 9-19.

The basic method of mixing was by a two stage process, with stepwise addition of ingredients during the first stage. Sulfur and accelerators were added to the rubber mixture in the second stage. The method used in the first stage was varied with respect to the technological factors of time, temperature and rotor speed. The second stage was always the same.

The order of mixing of tread compounds is shown in Table I.

The method used in the second mixing stage was always the same, as follows:

1.  $\frac{1}{2}$  of the mixture from stage 1 + the accelerators (in paste form).
2. The remaining  $\frac{1}{2}$  of the mixture from stage 1, + sulfur.

The total time of mixing in the second stage was 3 minutes. The ratio of rear to front rotor speeds was 50/42 rpm. The temperature of the final mixture at unloading time was 100–105° C.

TABLE I  
ORDER OF FIRST STAGE OF MIXING OF TREAD COMPOUNDS

Time of loading from start of process, min

Total time of processing in first stage, min <sup>1</sup>	SKS-30A +rosin +sine oxide +oleic acid +other small loadings + $\frac{1}{2}$ of furnace black	$\frac{1}{2}$ of furnace black +black petrodatum	$\frac{1}{2}$ of channel black	$\frac{1}{2}$ of channel black	Final time	Rear rotor speed, rpm
9	0	2	4	6	9	50
8	0	2	4	6	8	63
6	0	2	3	4	6	80
4	0	1	2	3	4	100
3.5	0	1	2	2.5	3.5	100
3	0	1	1.5	2	3	100
2.5	0	0.75	1.15	1.45	2.5	100
2	0	0	0	0.5	2	100
1.5	0	0	0	0.5	1.5	100

Control compounds were prepared using 9 minutes for the first stage with a rotor speed ratio of 50/42 rpm, and a final temperature of 100–105° C. The second stage required 3 minutes and the final temperature was also 100/105°C. The degree of dispersion and the physical-mechanical properties of the vulcanizates of the controls did not differ from those obtained in industrial preparations.

The effect of high temperature was studied at a rotor speed ratio of 100/84 rpm. Steam heating was sometimes used.

Typical tire industry compounds containing domestic synthetic rubbers were studied; tread compounds of butadiene-styrene rubber, SKS-30A in the first part of the report, and tread compounds of SKS-30A and SKS-30AM (oil-extended) as well as carcass compounds of sodium-butadiene rubber, SKB, in the second and third parts of the report.

The quality of mixing (degree of dispersion of black) was judged by microscopic analysis of the compounds after removal from the second stage of mixing. The measure of quality of dispersion was the area occupied by undispersed black in the visible field of a microscope at 100 X magnification.

The properties of the compounds and their vulcanizates were determined by the usual methods, all tests being made in duplicate or triplicate.

In this work it was kept in mind that the mixing process in the laboratory and in industry should be carried out under the same environmental conditions.

## EXPERIMENTAL

INFLUENCE OF TECHNOLOGICAL FACTORS IN THE MIXING  
PROCESS ON DISPERSION OF INGREDIENTS AND ON  
SPEED OF MIXING

*Temperature of mixing.*—Different points of view exist in the literature<sup>3,6,8</sup>. This is explained by the fact that the data were obtained under different technological conditions (mill mixing, mixer mixing, using different rubbers, using different order of mixing ingredients, different starting temperatures).

TABLE II

DISPERSION OF BLACK (AFTER SECOND STAGE OF MIXING) AS A FUNCTION OF THE TIME OF MIXING AND TEMPERATURE OF RUBBER MIXTURE IN THE FIRST STAGE OF THE PROCESS (RATIO OF ROTOR SPEEDS, 63/53 RPM; PRESSURE ON MIXTURE, 1.5–1.7 KG/CM<sup>2</sup>)

Preparation time in first stage, min	Values of black dispersion for given final temperature, ° C, of the first stage of mixing								
	97–102	120	130	140	145	150	160	165	Average
9	9.8	—	9.3	9.4	—	9.5	10.0	10.1	9.7
6	12.2	12.1	—	11.8	11.8	12.4	12.8	12.9	12.4
5	—	14.2	—	13.1	14.1	13.1	13.8	13.8	13.6
4	16.3	—	16.4	16.2	—	16.8	17.2	18.0	16.7

The results of our experiments are given in Table II and Figure 1. In these experiments the lowest temperature range of rubber mixtures was 95–105° C. This is the optimum temperature range used in industry for obtaining a compound of the required quality.

The data show that at temperatures up to 140° C the dispersion of carbon black remains practically unchanged. At 160–165° C there is some tendency



FIG. 1.—Dispersion of carbon black in mixtures as a function of final temperature of rubber mixture (rear rotor speed, 63 rpm). Abscissa—Temperature of rubber mixture, ° C; ordinate—Degree of dispersion of black. 1—Time of mixing, 4 minutes; 2—Time of mixing, 6 minutes; 3—Time of mixing, 9 minutes.

toward worse dispersion, especially at short mixing times. The important factor in increasing dispersion of black is increase in processing time.

The data obtained agree to a satisfactory degree with the theory of the process of mixing viscous materials. As is known<sup>9</sup>, the completeness of mixing of the mass, while constant pressure is maintained during the process of dispersing the black in the rubber, depends on the frequency of dividing the mixture in order to cause the formation of maximum contact area between the

TABLE III  
DISPERSION OF CARBON BLACK IN COMPOUNDS AS A  
FUNCTION OF ROTOR SPEED

Total time of first stage of mixing proce- ss, min	Time of each step in loading process, from start, min				Final temp. °C	Dispersion of black	Rear rotor speed, rpm
	Step 1	Step 2	Step 3	Step 4			
9	0	2	4	6	108	9.2	50
6	0	2	3	4	105	12.2	50
4	0	1	2	3	102	16.9	50
9	0	2	4	6	115	9.3	63
6	0	2	3	4	113	9.3	63
4	0	1	2	3	102	16.3	63
9	0	2	4	6	130	9.6	80
6	0	2	3	4	124	9.7	80
4	0	1	2	3	119	10.1	80
9	0	2	4	6	163	10.3	100
6	0	1	3	4	152	10.1	100
4	0	1	2	3	128	9.7	100

rubber and the pigment. An increase in temperature does not produce this increase in surface contact and therefore does not cause better infiltration of black into the rubber which would lead to an increased rate of dispersion. In the mixing process the temperature constantly rises, the viscosity of the rubber decreases and the condition exists for penetration of large unpulverized agglomerates of powdery pigment into the rubber. Therefore, under the conditions of this experiment, the dispersion of the black decreases at temperatures above 140° C. From this it can be concluded that the stiffer the mixture, the better the degree of dispersion.

*Speed of rotation of the rotors.*—The effect of increase of rotor speed on the speed and the degree of dispersion of black (Table III) was studied at four rotor speed ratios (50/42, 63/53, 80/67, 100/84, rpm). The time of mixing varied from 9 to 4 minutes.

From Table III it can be seen that the rubber temperature increases with increasing rotor speed. For a given mixing time (9 minutes), increase of rotor speed did not increase dispersion of black: at a speed of 100 rpm there was a tendency toward worse dispersion. There is practically no change in degree of dispersion when the mixing time is decreased proportionally to the increase in rotor speed. Therefore, we think that by increasing the number of rotations in a mixing cycle it is possible to decrease the mixing time without decreasing

TABLE IV  
DISPERSION OF BLACK AS A FUNCTION OF TIME OF MIXING AND  
TEMPERATURE OF MIXING (ROTOR SPEED RATIO, 100/84 RPM)

Total time of first stage of mixing proce- ss, min	Time of each step in loading process, from start, min				Final tem- perature of mixture, °C	Dispersion of black
	Step 1	Step 2	Step 3	Step 4		
4	0	1	2	3	128	9.7
4	0	1	2	3	170	10.2
3.5	0	1	2	2.5	125	9.9
3.5	0	1	2	2.5	165	10.2
3	0	1	1.5	2.0	122	10.2
3	0	1	1.5	2.0	160	10.6
2.5	0	0.75	1.15	1.45	150	10.1

the quality of the mixture when using stepwise addition of ingredients. The stepwise addition in Table III was carried out by adding all ingredients plus  $\frac{1}{4}$  of the black in Step 1, and the remaining black in the other three steps.

*The order of loading materials.*—In the experiments which were made with increased rotor speeds there was noticed an absence of coarse particles. We think this is explained by the short time of action of compression forces between

TABLE V

DISPERSION OF BLACK IN A COMPOUND BY ONE STEP LOADING OF ALL INGREDIENTS (ROTOR SPEED RATIO, 100/84 RPM)

Total time of first stage of mixing process, min	Time of each step in loading process, from start, min		Final temperature of mixture, °C	Dispersion of black
	Step 1	Step 2		
2	0	0.5	145	10.5
1.5	0	0.5	137	11.3

an edge of the rotor and the wall of the chamber. Additional experiments were made on varying the time at which the separate portions of black were added (Table IV).

The method of mixing by adding all the ingredients in one step has also been studied (Table V).

Table IV shows that as in previous experiments with the same mixing time, the increase of temperature to 165–170° C makes the dispersion somewhat worse.

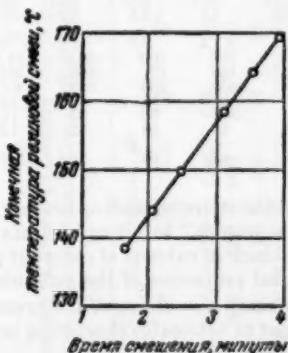


FIG. 2.—Change of temperature of rubber mixtures with time of mixing (rear rotor speed, 100 rpm).  
Abcissa—Mixing time, minutes; ordinate—Final temperature of rubber mixture, °C.

By shortening the mixing time in the first stage from 4 to 2.5 minutes, no appreciable change in black dispersion was found. We think this can be explained by the more efficient exchange of contacting surfaces caused by the more frequent loadings of black and by the decrease in idle time of rotation between the end of one mixing cycle and the start of the next. Operation by the method of mixing in which the time of mixing of separate portions was decreased under the industrial conditions of NIIShP, in slow speed mixers, gave positive results and confirmed our conclusions.

In one-step loading of all materials, 2 minutes of first stage mixing (Table V) was entirely adequate. The dispersion of the black in a 1.5 minute run was somewhat worse. From our point of view it can be made better by adding all of the ingredients at one time as has been done in foreign countries. This requires a larger outlet on the loading hopper.

The results given in Tables IV and V and Figure 2 prove that with shortened mixing time the final temperature of the mixture is lower. Therefore, to obtain lower temperatures of rubber mixtures with increased speed of rotation, the one step process of loading appears to be more effective.

*Pressure of mixing.*—The closed mixer has a sliding ram in the upper part of the mixing chamber which operates from a pneumatic cylinder. The total force on the ram, which is in turn transmitted to the mixture, can be calculated from the size of the piston and the air pressure in the cylinder. At the time of operation of the mixer, the ram can be under pressure or floating free. These experiments were done in the laboratory and under industrial conditions in the standard slow speed mixer. The results are given in Table VI.

TABLE VI  
CHARACTERISTICS OF RUBBER COMPOUNDS PREPARED UNDER DIFFERENT PRESSURES,  
AND PHYSICAL-MECHANICAL PROPERTIES OF THE VULCANIZATES (ROTOR SPEED  
RATIO, 100/84 RPM)

Property or condition	Method of loading ingredients							
	Stepwise (0, 1, 2, 2.5 min from start)				One step loading (0, 0.5 min from start)			
Plasticity of rubber, Karrer (B. F. Goodrich)	0.31	0.31	0.51	0.51	0.31	0.31	0.51	0.51
Mixing time, minutes	3.5	3.5	3.5	3.5	2	2	1.5	1.5
Pressure on mixture, kg/cm <sup>2</sup>	0.7	1.4	0.7	1.4	0.7	1.4	0.7	1.4
Dispersion of the black	10.3	10.5	10.2	10.6	11.1	10.5	13.2	11.3
Tensile strength, kg/cm <sup>2</sup>	188	186	171	160	161	172	159	170
Elongation, %	654	663	650	680	670	675	650	680
Residual elongation, %	17	16	18	20	20	19	19	20
Modulus, 300% elong.	70	64	70	70	70	71	64	70
Rupture resistance, kg/cm <sup>2</sup>	57	58	53	52	52	58	52	56
Resistance to crack growth, 10 <sup>3</sup> cycles	40	45	64	52	45	64	45	45

Table VI shows that in the stepwise loading process, an increase of the pressure on the rubber mixture from 0.7 to 1.4 kg/cm<sup>2</sup> has no appreciable effect on the degree of dispersion of black in rubbers of different plasticity or on improvement of physical-mechanical properties of the vulcanizates.

Under industrial conditions, a doubling of the pressure on the rubber (from 0.5 to 1 kg/cm<sup>2</sup>) did not lead to noticeable shortening of mixing time or improvement of dispersion.

When using one step loading of ingredients, except for delayed addition of  $\frac{1}{2}$  of the carbon black, an increase of pressure causes better dispersion of the black and shortening of the mixing time. The dispersion of the black equals that obtained by longer mixing with stepwise addition of ingredients.

#### Conclusions.—

1. The dispersion of black in rubber is not accelerated by increasing the temperature of mixing, but by faster mechanical agitation of the mass.
2. At mixing temperatures above 140° C, dispersion of black in rubber is somewhat worse because of the more plastic (softer) medium.

TABLE VII  
CHANGE OF DEFO PLASTICITY, KARRER PLASTICITY AND MOONEY VISCOSITY WITH MIXING TIME AND TEMPERATURE OF THE RUBBER MIXTURE. ROTOR SPEED RATIO, 100/84 RPM, EXCEPT FOR CONTROLS (\*), RUN AT 50/42 RPM

Property	Rubber	SKB, plasticity 0.35								SKS-30/A, Defo 325					
		SKS-30/A, Defo 450	9	3.5	3.5	3.5	9*	12	9	3.5	3.5	9*	12	9	3.5
Mixing time, min	12	9	3.5	3.5	3.5	3.5	9*	12	9	3.5	3.5	9*	12	9	3.5
Final temp. of rubber mixture, °C	195	175	170	160	133	100	165	165	155	145	115	100	175	165	125
Defo plasticity	1000	850	800	800	800	800	650	650	650	650	650	650	650	700	750
Mooney viscosity, 120	37	36	36	35	34	31	28	26	27	27	26	26	28	30	32
Karrer plasticity	0.37	0.38	0.38	0.39	0.39	0.4	0.5	0.49	0.49	0.49	0.51	0.51	—	—	—

3. With a given method of loading, the time of mixing is inversely proportional to the rotor speed.

4. An increase of rotor speed prevents the formation of agglomerates of powdery pigments, shortens the working time when separate portions of ingredients are added in stepwise loading and makes possible mixing when ingredients are added in one step.

5. The method of one step loading of ingredients into the mixing chamber, together with a doubling of rotor speed, produces the required quantity of rubber compound in a minimum of time (1.5 to 2 minutes), at low temperature.

6. An increase of pressure on the mixture is the most effective with short mixing cycles, with the one step loading process, and when the mixing is done at low temperature.

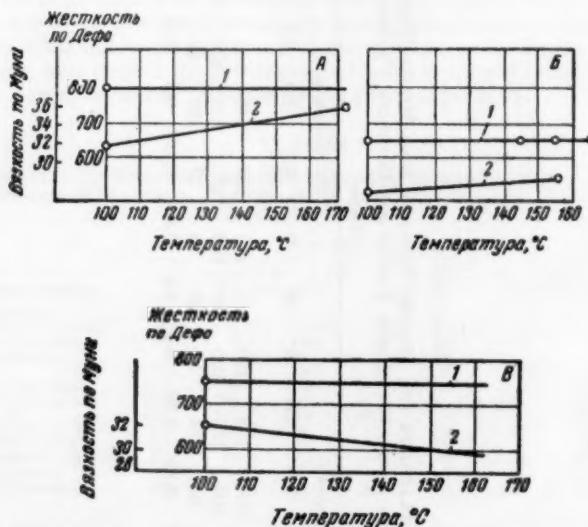


FIG. 3.—Change of Defo plasticity and Mooney viscosity with temperature of mixing (mixing time, 3.5 min). Abscissa for all curves—Temperature, °C; Ordinate for all curves—left, Mooney viscosity, right, Defo plasticity. 1—Defo plasticity; 2—Mooney viscosity. A—SKS-30A tread compound; B—SKB carcass compound; C—SKS-30AM tread compound.

#### THE INFLUENCE OF INCREASED TEMPERATURE IN THE MIXING PROCESS ON THE PROPERTIES OF COMPOUNDS AND VULCANIZATES OF SYNTHETIC RUBBERS

*Uncured compounds.*—The influence of increasing temperature was studied by changes in plasticity and in the elastic properties of the rubber compounds which characterize the behavior of the compounds in the preparation of intermediate products.

The changes in the plasticity of compounds as a function of temperature and mixing time are given in Table VII and Figure 3.

The data in Table VII show that an increase of temperature from 100 to 170° C in short cycles in the first mixing stage does not cause an appreciable change in the Defo or Williams plasticity. With an increase of mixing time

and at temperatures above 170° C, the SKS-30A compounds increase in hardness and decrease in plasticity while the SKS-30AM compound becomes softer. For the SKB compounds there is an insignificant change in plasticity with increase in temperature and mixing time.

The most sensitive indicator of the effect of high temperature of mixing on the toughness is the shear viscosity run on the Mooney viscometer<sup>10</sup>. With

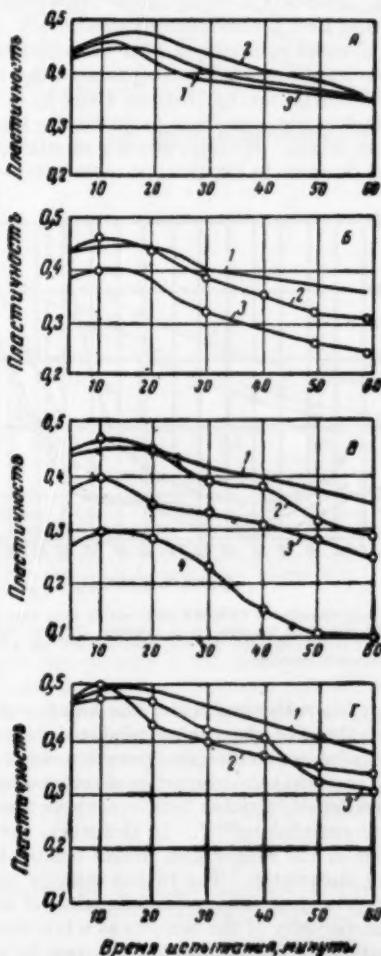


FIG. 4.—Change of Goodrich plasticity of SKS-30A compounds as a function of time of heating at 110° C. Compounds prepared at different temperatures and times of mixing. Abcissa for all curves—Time of heating, minutes; (Literal translation—Time of experiment, minutes). Ordinate for all curves—Plasticity. A—Mixing time, 3.5 min; 1—Control; 2—Final temperature of the mixture, 133°; 3—160°; B—Mixing time, 9 min; 1—Control; 2—Final temperature of the mixture, 160° c; 3—Final temperature of mixture, 171°; C—Mixing time, 12 min; 1—Control; 2—Final temperature of mixture, 160°; 3—Final temperature of mixture, 190°; 4—Final temperature of mixture, 193°; D—Mixture at 160°; 1—Mixing time, 3.5 min; 2—Mixing time, 9 min; 3—Mixing time, 12 min.

SKS-30A and SKB compounds the viscosity increases somewhat at higher temperatures, but it decreases with SKS-30AM.

Some peculiarities of high temperature mixing of synthetic rubbers noticed during these experiments should be mentioned. SKB compounds process equally at the different temperatures. SKS-30A compounds begin to stick to the rotors as temperature increases and become increasingly sticky at the higher temperatures. SKS-30AM compounds are easier to unload at the higher temperatures and they are shinier and smoother.

*Change of degree of scorch resistance.*—This was checked in the interval of 100–175°C mixing temperature and at mixing times of 3.5 to 12 minutes in the first stage. The experimental results (Figures 4 and 5) show that an increase in mixing temperature does not contribute to shortening the time period before scorch for short mixing cycles. With an increase of mixing time the influence of temperature on the decrease in plasticity is more noticeable (Figure 4C).

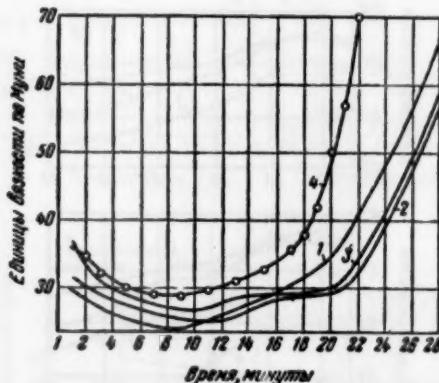


FIG. 5.—Change of Mooney viscosity of SKS-30A with mixing time (test temperature, 130°C). 1—Control; 2—Mixing time, 3.5 min, final temperature of mixture, 133°C; 3—Mixing time, 3.5 min, final temperature of mixture, 160°C; 4—Mixing time, 12 min, final temperature of mixture, 196°C. Abscissa: Time, minutes. Ordinate: Mooney viscosity.

*Change of viscosity of the rubber and rubber compounds.*—As mentioned above, an increase in temperature of the rubber mixtures decreases the viscosity. This change in viscosity has economic value since the cost of processing is lower.

Prolonged heating can affect the properties of compounds because of factors such as oxidative degradation, reaction between rubber and black and thermal structure formation or crosslinking<sup>11–12</sup>. In this work, the dependence of the viscous flow properties of the rubber and rubber compounds was studied by means of the Mooney viscometer. The rubber samples and compounds, prepared at different temperatures, did not contain sulfur or accelerators.

Figure 6 shows the viscosity of the samples as a function of temperature at constant time of heating in the viscometer. It can be concluded that the viscosity of the rubber and the rubber compounds definitely changes with temperature. The viscosity of the rubber compounds is greater than that of the rubber because of the presence of pigments, largely, black. At high temperatures the difference in viscosity between the different rubbers is reduced. Therefore, the use of the tougher butadiene-styrene rubbers with fast mixing is

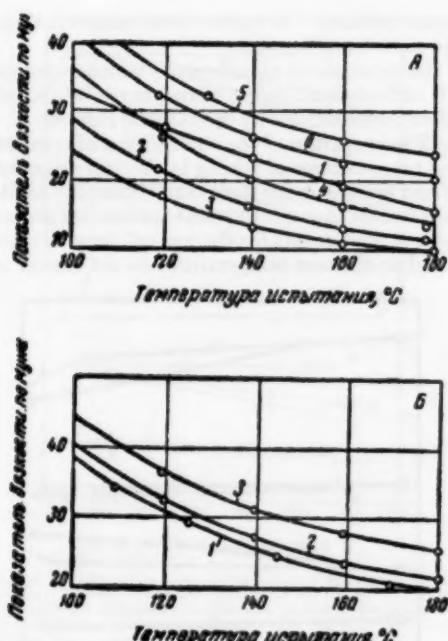


FIG. 6.—Change of Mooney viscosity of rubbers and rubber mixtures with test temperature in the viscometer (5 min test). Abscissas, both curves; Test temperature, °C. Ordinate, both curves; Mooney viscosity. A—Change of viscosity of rubber and rubber mixtures with temperature; 1—Natural rubber; 2—SKS-30AM; 3—SKB; 4—SKS-30A; 5—SKS-30AM mixture; 6—SKS-30A mixture; B—Change of viscosity of SKS-30A mixtures prepared at different mixing temperatures; I—Control; 2—3.5 min mixing time at 165°; 3—8 min mixing time at 175°.

economically advantageous. The viscosity of compounds prepared at higher temperatures (Figure 6B) changes in the same manner as the control. From this it can be concluded that such mixtures are softened by processing and behave analogously to compounds prepared in the normal manner. The fact that compounds prepared at high temperatures soften in the same manner as the control when heated in the Mooney viscometer for 5 minutes, proves the absence of appreciable structure change in the rubber polymer. The increase in viscosity begins only after 6 minutes at 180° C for SKB and after 10–12 minutes for

TABLE VIII  
ADHESIVITY OF RUBBER COMPOUNDS AT DIFFERENT  
MIXING TEMPERATURES

Condition or property	Type of compound								
	SKB carcass, plasticity, 0.49			SKS-30A tread, plasticity, 0.484			SKS-30AM, tread, plasticity, 0.45		
Mixing time, min	9	4	3.4	9	4	3.5	9	4	3.5
Final temperature of mixture, °C	100	147	152	108	160	170	108	168	167
Adhesivity on Ber instrument	860	990	990	1215	1720	1525	730	720	710

the butadiene-styrene rubbers. In rubber black mixtures this change becomes noticeable after 16 minutes of heating.

The results of the experiments on adhesivity as measured on the Ber instrument (Table VIII) indicate that higher mixing temperatures with short mixing cycles has little effect on the adhesivity of synthetic rubbers.

*Vulcanizates.*—The properties of the vulcanizates of compounds prepared at different times and temperatures of mixing in the first stage were evaluated by results obtained from testing under static and dynamic conditions.

Figures 7, 8 and 9 show that the physical-mechanical properties of the compounds (cured at the optimum cure for the control) from mixtures prepared with different rubbers and at different temperatures do not change in the same man-

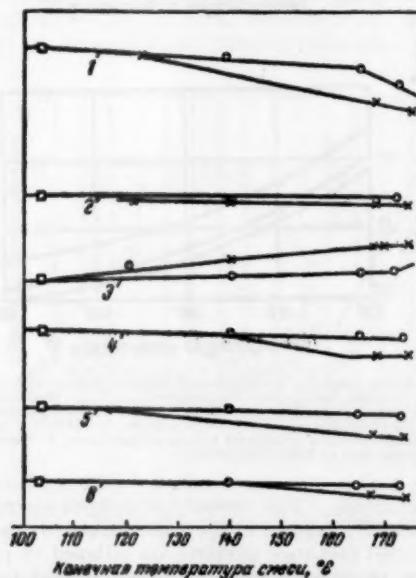


FIG. 7.—Dependence of physical-mechanical properties of vulcanizates on the mixing temperature (tread compound, SKS-30A). Absciss: Final temperature of the mixture, ° C. 1—Relative elongation; 2—Tensile strength; 3—Modulus, 300% elongation; 4—Rupture; 5—Relative elongation; 6—Resistance to bending, in thousands of cycles; □—Control; ○—Mixing time, 3.5 min; ×—Mixing time, 5 min.

Translator's note: In Figure 7, number 1 and 5 terms are identical. This is probably an error and number 5 should be residual elongation.

ner. With short mixing cycles (3.5 to 4 minutes) in the 100–165° C temperature range, the physical-mechanical properties of the vulcanizates approach those of the control. Such properties as tensile strength, rupture resistance, Shore hardness, flex resistance to bending and to stretching, stay within the limits obtained with the control.

The characteristic which is specific for the vulcanizates prepared by shorter and higher temperature mixing cycles is the small decrease in relative and residual elongation for SKS-30A and SKB compounds. The SKS-30AM compounds remain unchanged in this property. Increase in mixing time leads to a further decrease of this property. This property of SKS-30AM also decreases with longer mixing time, but to a lesser degree.

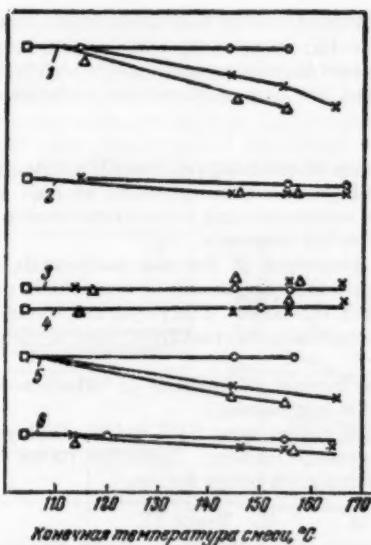


FIG. 8.—Dependence of the physical-mechanical properties of vulcanizates on the mixing temperature (carcass compound, SKB). Abscissa: Final temperature of the mixture, °C. 1—Relative elongation; 2—Tensile strength; 3—Modulus at 300% elongation; 4—Residual elongation, tear; 5—Resistance to stretching, in thousands of cycles; □—Control; ○—3.5 min mixing; ×—4 min mixing; Δ—5 min mixing.

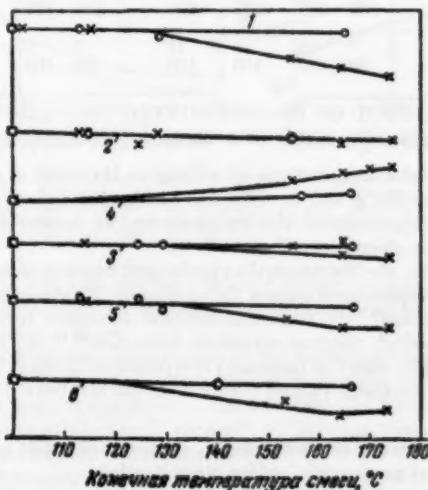


FIG. 9.—Dependence of the physical-mechanical properties of vulcanizates on the mixing temperature (tread compound, SKS-30AM). Abscissa: Final temperature of the mixture, °C. 1—Relative elongation; 2—Tensile strength; 3—Modulus at 300% elongation; 4—Residual elongation, tear; 5—Resistance to bending, in thousands of cycles; □—Control; ○—Mixing time, 3.5 and 5 min; ×—Mixing time, 8 min.

At high mixing temperatures the modulus and the resistance to wear and to ozone cracking (Table IX) increase for butadiene-styrene rubbers. This increase is greater the longer the mixing period at the high temperature. With the SKB carcass compound, the increase of modulus with temperature is negligible.

*Conclusions.—*

1. A thorough study of synthetic rubbers SKS-30A, SKB, SKS-30AM and of raw compounds of these rubbers prepared at high mixing temperatures proved that to obtain compounds and vulcanizates having the required properties short mixing cycles are necessary.
2. Plastic-elastic properties of the raw compounds obtained by mixing 3.5–4 minutes at high temperatures and of compounds prepared by standard methods are practically the same. The physical-mechanical properties of the vulcanizates are not essentially different from those of vulcanizates prepared by the usual methods.
3. The noticeable increase in modulus of butadiene-styrene rubber compounds can be useful in some cases.
4. The oil-extended rubber type, SKS-30AM, displays greater heat resistance than the other synthetic rubbers. Therefore, its use in industry with high-temperature, fast-mixing gives better results.

TABLE IX  
RESISTANCE OF RUBBER TO OZONE CRACKING

Condition	Rubber compound							
	SKS-30A				SKS-30AM			
Mixing time, min.	9	3.5	3.5	9	9	3.5	3.5	9
Final temperature of mixture, °C	100	130	150	170	100	125	163	170
Time before start of cracks, min	7	10	16	17	9	9	13	15
Rotor speed, rpm	50	100	100	100	50	100	100	100

THE EFFECT OF HIGHER MIXING TEMPERATURES  
ON THE KINETICS OF VULCANIZATION

*The effect of higher temperatures of mixing on the speed of vulcanization as a function of the quantity of sulfur.*—As was mentioned before, at higher mixing temperatures the elasticity of the vulcanizates, as measured by relative and residual elongation, decreases (Figures 7–9).

It is known from the literature that prolonged heating of sulfurless synthetic rubbers at high temperatures causes, depending on the structure of the polymer, oxidative degradation<sup>11,14,15</sup>, three-dimensional structure formation under the influence of oxygen<sup>11,15</sup>, thermal structure formation<sup>12,16</sup>, or, reaction of rubber with black<sup>13,17</sup>. The effect of increased temperature in short time mixing processes on domestic synthetic rubber compounds has not been described in the literature.

To explain the cause of these effects, compounds made by three modifications with different amounts of sulfur were studied:

1. With standard recipe and control mixing method.
2. With standard recipe, at double the control rotor speed, at high temperature.
3. Same as modification 2, but with less sulfur present.

Figure 10 gives the results obtained on the three SKS-30A compounds at different vulcanization times. Analogous results were obtained with SKB and SKS-30AM compounds. Figure 10A shows that tensile strength does not change appreciably for any of the compounds. The elastic properties change considerably. For compounds prepared at high temperature (Curve 2), the elastic properties are lower than those of the control. For the lower sulfur compound prepared at high temperature, the elastic properties are higher than those of the control. It can also be seen that by high temperature mixing of

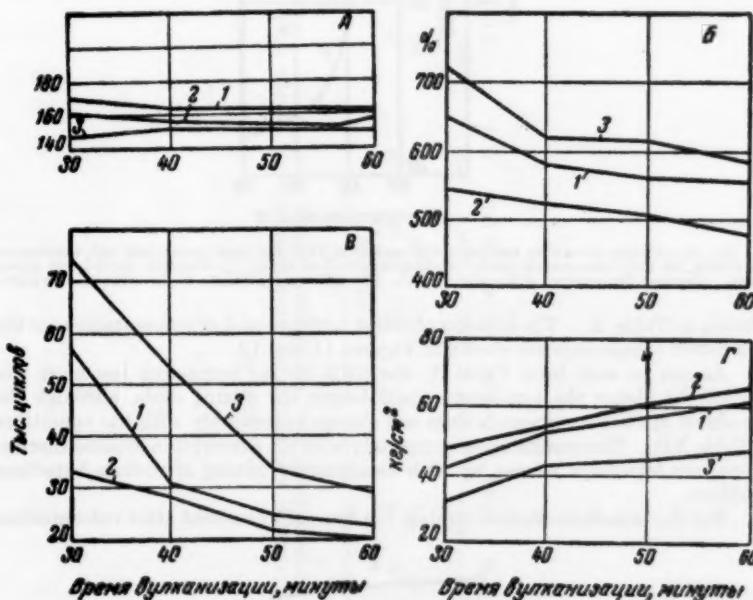


FIG. 10.—Dependence of physical-mechanical properties of vulcanizates on time of mixing and sulfur content (tread compound, SKS-30A). Abscissa, all curves; Time of vulcanization, min. Ordinate: graph C, Thousands of cycles; graph D, kg/cm<sup>2</sup>. A—Tensile strength; B—Relative elongation; C—Flex resistance, stretching; D—Modulus at 300% elongation; 1—Control, 2% sulfur; 2—3.5 min mixing time, 170°, 2% sulfur; 3—3.5 min mixing time, 170°, 1.7% sulfur.

rubber and black, vulcanizates are obtained whose properties are near to those obtained from the control mixed under the usual conditions, when comparison is made at long curing times.

*Effect of higher mixing temperature on the kinetics of addition of sulfur.*—A number of authors have noticed that structure changes can take place in synthetic rubber at high temperature. In this case the oxidation process takes place by formation of C—O—C groups<sup>11</sup>, or thermal crosslinking takes place between chains to replace double bonds by C=C<sup>12,13</sup>.

Thus, in high temperature mixing, with the presence of some already formed structure and some loss of unsaturation, it can be expected that less sulfur would be required to obtain soft vulcanizates that would be required for the compounds prepared by the control method.

The results of the comparison study of the kinetics of addition of sulfur are

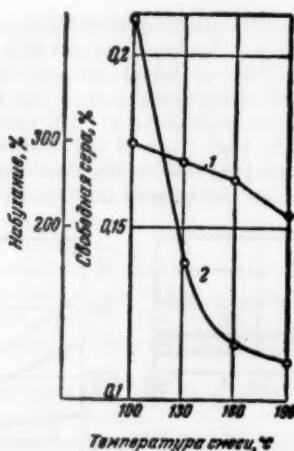


FIG. 11.—Change in swelling and free sulfur content of SKS-30A tread compounds with temperature of mixing (40 min vulcanization time). 1—Swelling; 2—Free sulfur; □—Control; ○—3.5 min mixing time. Abcissa; Temperature of the mixture, °C. Left ordinate; Swelling. Right ordinate; Free sulfur.

shown in Table X. The kinetics of sulfur addition and of vulcanization for the SKS-30A compounds are shown in Figures 11 and 12.

As can be seen from Table X, the SKB rubber compound has more free sulfur the higher the temperature and longer the mixing cycle, although the modulus of these compounds does not change appreciably with the conditions (Table XI). The results agree completely with the assumption of some thermal structure formation caused by high temperature mixing of sodium-butadiene rubber.

For the butadiene-styrene rubber, the free sulfur content after vulcanization

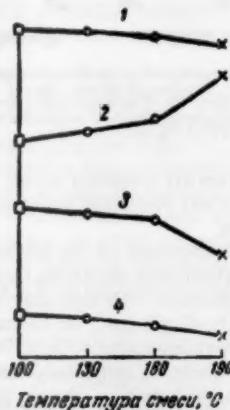


FIG. 12.—Change of physical-mechanical properties of the same vulcanizates as in Figure 12. 1—Tensile strength; 2—300% modulus; 3—Relative elongation; 4—Residual elongation; □—Control; ○—3.5 min mixing time; ×—12 min mixing time. Abcissa; Temperature of the mixture, °C.

TABLE X  
SULFUR CONTENT OF VULCANIZATES AS A FUNCTION OF METHOD OF MIXING (ROTOR SPEED RATIO  
FOR CONTROL, 50/42 RPM; FOR OTHERS, 100/84 RPM)

Condition or property	SKB	SKS-30A				SKS-30AM			
		9	3.5	3.5	9	9	3.5	3.5	9
Mixing time, min	9	3.5	3.5	9	9	3.5	3.5	3.5	9
Rotor speed, rpm	50	100	100	100	50	100	100	50	100
Final temp. of rubber mixture, °C	105	132	152*	165*	103	130	160*	170*	100
Free sulfur, %	0.18	0.17	0.23	0.24	0.21	0.14	0.115	0.11	0.14

\* Mixture was steam heated.

is less for high temperature mixing of SKS-30A and SKS-30AM (Table X, Figure 11). These vulcanizates are characterized by a lower degree of swelling (Figure 11).

We conclude that high temperature mixing of butadiene-styrene rubber compounds appears to activate the process of addition of sulfur during the later stages of processing. This phenomenon could be explained by scission of the polymer chain with the formation of free radicals which can react with elemental sulfur. This explanation has been assumed by B. A. Dogadkin<sup>16</sup>, V. A. Kargin and G. L. Slonimskii<sup>18</sup>.

TABLE XI  
CHANGE OF MODULUS OF SKB CARCASS COMPOUND  
WITH MIXING METHOD

Mixing time, rubber mixture, min	Final temp. of °C	Modulus, elongation			
		50%	100%	150%	200%
9	105	15	28	41.5	54
3.5	132	14.2	26.5	40.5	52.5
3.5	152	14.8	28	41.5	53.5
9	165	13	25.1	39	50

### CONCLUSIONS

1. The work conducted confirms the expediency of using fast mixing methods for synthetic rubbers.
2. It is shown that future improvement may be obtained by using one step loading of all ingredients in the mixer, combined with greater pressure on the mixture and faster rotor speed.
3. We recommend the wide introduction, in production, of the two stage mixing process with increased rotor speed in the first stage.
4. In a factory producing two million tires a year, this decreases the investment by 7.5 million rubles and cuts operating expenses by 2 million rubles per year.

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- Translator's notes: There is no mention of References 1, 2, 4, 5, and 7 in the text. The Williams plasticity data referred to on page 914 does not appear in Table VII or elsewhere in the text.

# SURFACE HEATING BY FRICTION AND ABRASION BY THERMAL DECOMPOSITION \*

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## INTRODUCTION

The question of what temperatures may arise at the boundary between pavement and tread must be answered if we are to determine the influence of these temperatures in connection with the problem of abrasion of rubber, and if we are to determine whether abrasion is to be considered as essentially due to the tearing out of particles or to the oxidative depolymerization of the highly heated surface layer. The conception of the oxidative decomposition of the rubber molecule is important if temperatures are reached under given conditions of abrasion, which lie above the decomposition temperature of rubber. Reliable measurements of friction temperatures are not available, and are likely to be difficult to obtain with satisfactory accuracy, as is indicated in the following. Nevertheless, in order to arrive at an idea of friction temperature which may be expected under different driving conditions, an attempt will be made, in the following work, to carry through a mathematical appraisal based on phenomenological theories of heat conduction. This estimate will at least give the relative magnitude of significant values for friction temperatures with tires, and point out the most important factors which determine the friction temperatures.

For the case when the decomposition temperature of rubber is exceeded, an idea of the abrasion promoted by this decomposition of the rubber molecules will be deduced for certain idealized conditions.

## GENERAL PRINCIPLES

*Stationary (steady) state.*—Where a heat current  $i$  flows in a medium whose heat conductivity is  $\lambda$  and whose thickness is  $d$  and area  $F$  (Figure 1), the temperature  $T_\infty$  will exist on the surface after a stationary or equilibrium state has been reached (defined by  $dT/dt = 0$ ) according to Equation (1), provided that the boundary condition,  $T = T_0$  (constant temperature) at  $x = d$  is maintained.

$$T_\infty - T_0 = \frac{i \cdot d}{F \cdot \lambda} \\ = j \cdot \frac{d}{\lambda} \quad (1)$$

In the following work,  $T_0$  will not always be introduced in the equations, but instead will be assumed to be zero. In other words, the prevailing street temperature is to be added to the attained temperature.

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe, from Kautschuk und Gummi, Vol. 10, No. 12, pages WT 302-307, December, 1957.

TABLE I  
LIST OF SYMBOLS AND CONCEPTS

Symbol	Definition	Dimension
$\lambda$	Thermal conductivity	cal/cm sec degree
$k$	Thermal diffusivity	cm <sup>2</sup> /sec
$Q$	Heat quantity	cal
$i = \frac{Q}{t}$	Heat current	cal/sec
$t$	Time	sec
$j = i/F$	Heat current density	cal/cm <sup>2</sup> sec
$R$	Thermal resistance	degrees
$F$	Contact area	cal/cm <sup>2</sup> sec
$\tau$	Time interval	sec
$T$	Temperature	°C
$\mu$	Coefficient of friction	Dimensionless
$p$	Load	kg/cm <sup>2</sup>
$v$	Velocity	cm/sec
$c, l, z_0$	Lengths	cm
$E_s$	Specific energy of decomposition	cal/g
$\rho$	Density	g/cm <sup>3</sup>

*Application to friction phenomena.*—In the case of friction processes which will be considered in the following, the heat current originates in the boundary layer between two bodies, the rubbing body (Medium 1) and the base which is rubbed (Medium 2). In this case the heat current density is given by Equation (2).

$$j = \mu \cdot p \cdot v \quad (2)$$

In this equation,  $v$  is the relative velocity of Medium 1 with respect to Medium 2.



FIG. 1.—Illustration for Equation (1).

At first, for the sake of simplicity, we assume a closed contact surface, which we can think of as being realized by two concentric cylinders (see Figure 2).

Then when we make the assumption that the radii of the cylinders are very large compared with the thickness of the layers  $d_1$  and  $d_2$ , the analysis may be regarded as applying to a plane. Furthermore, the axial lengths of the cylinders shall be considered large compared with  $d_1$  and  $d_2$ , so that, by disregarding edge effects, Equation (1) can be applied for the equilibrium condition. The friction

temperature at the boundary is accordingly

$$\begin{aligned} T_1 &= j_1 \cdot \frac{d_1}{\lambda_1} \\ T_2 &= j_2 \cdot \frac{d_2}{\lambda_2} \end{aligned} \quad (1a)$$

if the portion of the specific heat current flowing in Medium 1 is  $j_1$  and the portion in Medium 2 is  $j_2$ .

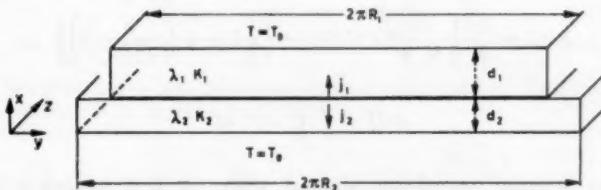


FIG. 2.—Two concentric cylinders, depicted with linear coordinates to represent an endless, closed contact surface.

From the self-evident condition that  $T_1 = T_2$ , a distribution law for this case is given by Equation (3).

$$\begin{aligned} j_1 &= j \cdot \frac{1}{1 + \frac{d_1 \cdot \lambda_2}{\lambda_1 \cdot d_2}} \\ j_2 &= j \cdot \frac{1}{1 + \frac{d_2 \cdot \lambda_1}{\lambda_2 \cdot d_1}} \end{aligned} \quad (3)$$

It may be seen from this distribution law how strongly the friction temperature is influenced by the rubbed base and particularly by its thermal resistance,

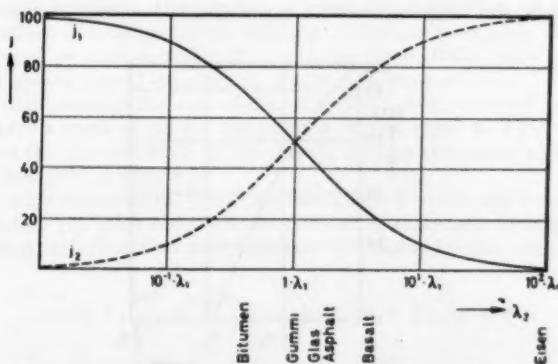


FIG. 3.—Heat current components  $j_1$  and  $j_2$  as a function of the thermal conductivity of the rubbed base, (Bitumen, bitumen; Gummi, vulcanized rubber; Glas, glass; Asphalt, asphalt; Basalt, basalt; Eisen, iron.)

$R_2 = d_2/\lambda_2$ . Figure (3) shows the specific heat current  $j_1$  as a function of the thermal conductivity of the rubbed base, for the special case  $d_1 = d_2$  and for rubber as the rubbing member with thermal conductivity  $\lambda_1$ . In the case where  $\lambda_2 = \lambda_1$ , 50 per cent of the total heat current flows in Medium 1 and 50 per cent in Medium 2. When  $\lambda_2 = 100\lambda_1$  only 0.9 per cent of the total heat current flows in Medium 1.

*Unsteady state.*—If a heat current  $j_1$  flows for only a finite period of time,  $\tau_p$ , we have the case of a heat current pulse so that a temperature distribution<sup>1</sup> is built up in a medium whose thermal diffusivity is  $k$  in accordance with Equation (4).

$$T(x) = \frac{2j_1}{\lambda} \left\{ \sqrt{\frac{k\tau_p}{\pi}} e^{-x^2/4k\tau_p} - \frac{x}{2} \left[ 1 - \phi \left( \frac{x}{\sqrt{4k\tau_p}} \right) \right] \right\} \quad (4)$$

$$\phi(\xi) = \frac{2}{\pi} \int_0^\xi e^{-z^2} dz \quad (4a)$$

$\phi(\xi)$  is the Gaussian probability integral, when the heat current is in the  $x$  direction.

Equation (4) may be written with Equation (6) in the form:

$$T(x) = T(x=0) \cdot \left\{ e^{-x^2/4k\tau_p} - \frac{x\sqrt{\pi}}{\sqrt{4k\tau_p}} \left[ 1 - \Phi \left( \frac{x}{\sqrt{4k\tau_p}} \right) \right] \right\}$$

$$= T(x=0) \cdot \sqrt{\pi} \cdot \text{ierfc}(\xi); \quad \xi = \frac{x}{\sqrt{4k\tau_p}} \quad (4b)$$

(The function  $\text{ierfc}(\xi)$  is tabulated; see Reference 1, for example.)

At the depth of a boundary layer given by Equation (5), the temperature drops to one-tenth of the surface temperature, as illustrated in Figure 4.

$$d_p = \sqrt{4k\tau_p} \quad (5)$$

In other words, the temperature field is practically localized in this boundary layer.

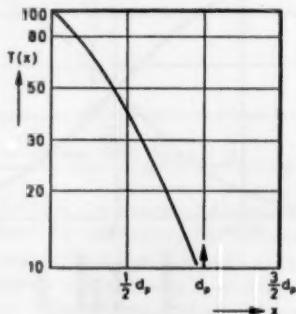


FIG. 4.—Temperature distribution curve for nonstationary heat current, according to Equation 4.

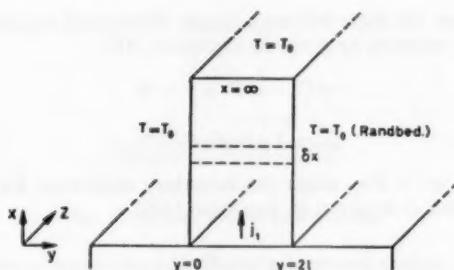


FIG. 5.—Two concentric rings, as the representation of a closed contact surface.

The temperature of the boundary surface calculated by Equation (4) for the case where  $x = 0$ , is given by Equation (6).

$$T(x = 0) - T_0 = j_1 \cdot \frac{d_p}{\lambda \sqrt{\pi}} = 2j_1 \sqrt{\frac{k \cdot \tau_p}{\pi}} \cdot \frac{1}{\lambda} \quad (6)$$

The same form of expression as is shown in Equation (1) is obtained here by replacing the layer thickness  $d$  with the "reduced boundary layer," as given in Equation (7).

$$d_p' = 2 \sqrt{\frac{k \cdot \tau_p}{\pi}} \quad (7)$$

When the heat current pulse of duration  $\tau_p$  arises from friction in the boundary layer between two media, we derive the distribution law expressed by Equation (8), deduced from Equations (3) and (7).

$$j_1 = j \cdot \frac{1}{1 + \sqrt{\frac{k_1 \cdot \tau_p}{k_2 \cdot \tau_p} \cdot \frac{\lambda_2}{\lambda_1}}} \quad (8)$$

*Finite contact surfaces, steady state.*—In case the assumption no longer holds that the surface dimensions of the rubbing bodies are very large compared to their thickness, we must consider the heat losses through the edges of the bodies in order to obtain a good estimate of the friction temperatures.

Let us first consider the case of closed surfaces, best pictured in ring form. Take however a finite width for the rubbing bodies, equal to  $2l$  in the  $y$  direction, so that the circumference of the rings  $z_0$  is large compared with the width  $2l$ . This is shown in Figure 5.

On the edge surfaces, the boundary condition  $T = T_0$  will be maintained. Then Equation (9) holds for a volume element of thickness  $dx$  at the position  $y = l$  in the equilibrium case and Equation (10) holds for the boundary conditions.

$$z_0 \cdot 2l \cdot \lambda_1 \frac{\partial^2 T}{\partial x^2} \delta x - \frac{\lambda_1}{l} (2z_0 + 4l)(T - T_0) \delta x = 0 \quad (9)$$

$$i_1 = (2z_0 + 4l) \frac{\lambda_1}{l} \int_0^\infty (T - T_0) \delta x \quad (10)$$

From Equation (9) there follows a simple differential equation in  $T$ , Equation (11) and its solution, as given in Equation (12).

$$aT'' - bT + c = 0 \quad (11)$$

$$T - T_0 = A \cdot e^{-\sqrt{b}/a x} \quad (12)$$

If we assume  $4l < 2z_0$ , using the boundary condition, Equation (10) we obtain the constant  $A$  as given in Equation (13).

$$A = \frac{i_1}{2z_0\lambda_1} \quad (13)$$

and thence the final solution in Equation (14).

$$T - T_0 = \frac{i_1}{2z_0\lambda_1} \cdot e^{-x/l} \quad (14)$$

For the surface temperature, we get when  $x = 0$ , the expression in Equation (15).

$$(T - T_0)_{x=0} = \frac{i_1}{2z_0\lambda_1} \quad (15)$$

If the specific heat current  $j_1 = \frac{i_1}{2z_0l}$  is put into Equation (15) we arrive at Equation (16).

$$(T - T_0)_{x=0} = j_1 \cdot \frac{l}{\lambda_1} \quad (16)$$

Here again is found the general form of Equation (1), where, in place of the layer thickness  $d_1$ , a sort of "boundary layer" of thickness  $l$  is used. Equation (16) may be interpreted thus: the heat losses through the edges cause a "virtual sink" for the heat current when  $x = l$ .

If the rubbing body is finite in the  $z$  direction, and we assume it to be square with sides of length  $2l$ , we may derive Equation (17) by

$$T - T_0 = \frac{i_1 \cdot \sqrt{2}}{8\lambda_1 l} \cdot e^{-\sqrt{2} \cdot (x/l)} \quad (17)$$

analogous calculations. Thus the boundary layer for this case is  $x_0 = 0.7l$ , and for the surface temperature we get the expression in Equation (18).

$$(T - T_0)_{x=0} = j_1 \cdot \frac{0.7l}{\lambda_1} \quad (18)$$

The finite extension in the  $z$  direction brings about a further shift of the virtual sink to the position,  $x = 0.7l$ . A strict mathematical treatment would have to take into account the temperature distribution in the  $y$  direction. This leads to a distribution in the form of a bell shaped curve, but the calculations are beyond the scope of this article.

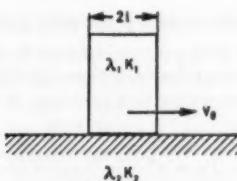


FIG. 6.—Rutting body of finite dimension.

*Sliding friction of a rutting body with finite contact surface; steady/unsteady state.*—After dealing in the previous section with a closed surface, we must now take into consideration in the case of a finite contact surface that, during the rutting process the surface of the rutting body comes in contact continuously with new, unwarmed surface of the rubbed base. We will consider in the following, the case of a sliding body with finite contact area, whose length in contact with the rubbed medium is \$2l\$ in the direction of sliding. See Figure 6.

If the relative velocity of the rubbed and rutting bodies is \$v\_0\$, then the pulse duration \$\tau\_{p\_2}\$ during which a heat current pulse \$j\_2\$ flows in a surface zone of the rubbed base of length \$2l\$, is \$\tau\_{p\_2} = 2l/v\_0\$, and the distribution law (see Equation (3)), is given in Equation (19) for the case when a stationary state exists in the rutted body.

$$j_1 = j \cdot \frac{1}{1 + \sqrt{\frac{(0.7l)^2 \cdot v_0 \cdot \lambda_2}{k_2 \cdot 2l \cdot \lambda_1}}} \quad (19)$$

Using Equation (16), we then derive the expression for the temperature of the boundary layer in Equation (20).

$$(T - T_0)_{z=0} = j \cdot \frac{0.7l}{\lambda_1 = 0.5\lambda_2 \sqrt{\frac{v_0 \cdot l}{k_2}}} \quad (20)$$

Equation (20) shows that the effect of the rubbed base (\$\lambda\_2\$) on the distribution of the heat current is greater, the greater the relative velocity \$v\_0\$. This effect

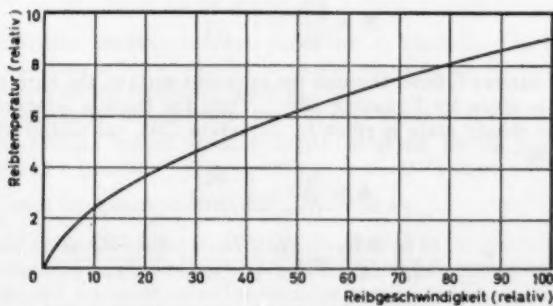


FIG. 7.—Friction temperature of a sliding body of finite extent as a function of sliding velocity. Ordinate: Friction temperature (relative). Abscissa: Sliding velocity (relative).

is such, that the friction temperature rises with increasing  $v_0$ , but not directly proportional to  $v_0$ , but in a first approximation to its square root,  $\sqrt{v_0}$ . Considering that  $j = \mu \cdot p \cdot v_0$ , it may be seen that the friction temperature with increasing velocity increases according to a function of the type shown in Equation (20a) and in Figure 7.

$$T - T_0 = C \cdot \frac{v_0}{1 + \sqrt{v_0}} \rightarrow C \cdot \sqrt{v_0} \quad (20a)$$

*Local temperature at contact bridges.*—Up to this point we have given all our attention to an ideal surface, that is a surface without any roughness. In the following, we will assume that the contact surface consists of alternating "bridges" and "gaps" (or elevations and depressions) the edge length of which is  $2l_s$ . (See Figure 8.)

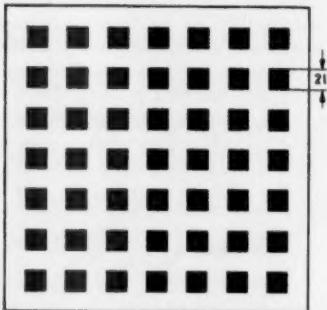


FIG. 8.—Model of a rough contact surface made up of square "bridges" and "gaps" of edge length  $2l_s$ .

The true contact area will accordingly be less than it appears, and in case the bridges and gaps alternate regularly, Equation (21) holds.

$$F_{\text{real}} = 0.25F_0 \quad (21)$$

Then there are  $N$  bridges per  $\text{cm}^2$  of area according to Equation (22).

$$N = \frac{\frac{1}{4}F_0}{4l_s^2} = \frac{2.5 \cdot 10^{-1}}{4l_s^2} \quad (22)$$

If a heat current  $i_1$  flows through the apparent surface, the current intensity in a bridge is given by Equation (23). Then the friction temperature for a bridge in the steady state is given by Equation (24), calculated by means of Equation (18)

$$i_b = \frac{i_1}{N} = \frac{i_1 \cdot 4l_s}{2.5 \cdot 10^{-1}} \quad (23)$$

$$T_{\text{stat}} = \frac{i_b}{4l_s^2} \cdot \frac{0.7l_s}{\lambda_1} = \frac{i_1 \cdot 0.7l_s}{2.5 \cdot 10^{-1} \lambda_1} = \frac{1.5 \cdot (2l_s) \cdot i_1}{\lambda_1} \quad (24)$$

The equilibrium temperature of a contact bridge increases in proportion to its length. If, however, we have to deal, as in case of a rolling tire, not with a

steady heat current, but with a current pulse of duration  $\tau_p$ , then for all bridges whose length

$$2l_s \gg d_p = 2\sqrt{k\tau_p}$$

the steady state will not be reached, but a friction temperature is found as given in Equation (25), based on Equation (6).

$$T_{R_1} = jb \cdot \frac{d_p'}{\lambda_1} = 4j_1 \frac{2d_p}{\lambda_1 \sqrt{\pi}} \quad (25)$$

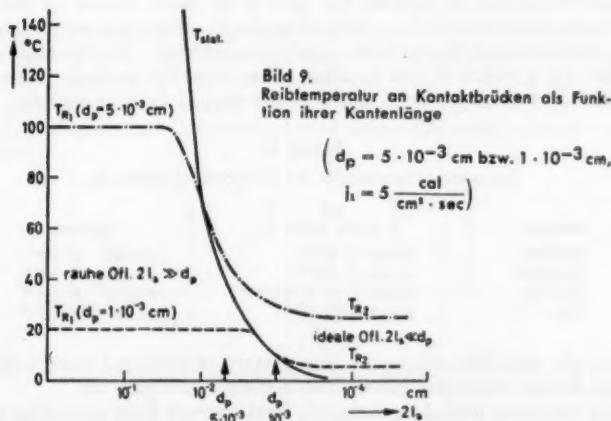


FIG. 9.—Friction temperature at contact bridges as a function of their edge length. rauhe Ofl.; rough surface; ideale Ofl.; ideal surface; bsw.; respectively.

For a smooth surface, that is  $2l_s \ll d_p$ , the maximum temperature reached will be given by Equation (26),

$$T_{R_2} = 2j_1 \cdot \frac{d_p}{\sqrt{\pi \cdot \lambda_1}} = \frac{1}{4} T_{R_1} \quad (26)$$

The transition between the two cases lies at  $2l_s = d_p$ . In other words: whether a surface is to be considered as smooth or rough for purposes of our theory depends on the boundary layer  $d_p$ .

Local overheating (temperature flashes) may occur in certain circumstances for contact bridges whose contact length is given by  $2l_s \geq d_p = 2\sqrt{2k\tau_p}$ . Figure 9 shows a practical example with  $d_p = 5 \cdot 10^{-3}$  cm, or  $1 \cdot 10^{-3}$  cm and  $j_1 = \frac{5 \text{ cal}}{\text{cm}^2 \text{ sec}}$  with the assumption that  $F_{\text{real}} = 0.25 F_0$ .

The solid curve shows the friction temperature to be expected for the steady state, calculated from Equation (24). The broken line curves are for the unsteady state, and are made up of the portions parallel to the abscissa calculated by Equations (25) and (26) together with a connecting section along the curve  $T_{\text{stat.}} = f(2l_s)$  calculated by means of Equation (24) in the region  $2l_s = d_p$ .

## PRACTICAL EXAMPLES FOR TIRES

In this section, using formulas derived in the preceding work, the friction temperatures will be estimated for tires under different driving conditions. Since the formulas provide only approximate evaluations, and since allowance must be made for certain parameters (such as the friction coefficient and slippage) the results must be regarded as showing only the order of magnitude of the friction temperatures which are to be expected. We will take asphalt as a typical street paving material since it shows thermal properties very similar to rubber. See Table II.

Basalt or concrete, since their thermal diffusivities and conductivities are about four times that of asphalt, will give in all cases, values for the friction temperature about two-thirds of that for asphalt. For purposes of comparison iron has been referred to as a base or rubbed material. Its thermal constants are greater by a factor of one hundred than those for asphalt. The friction temperature in this case will be about 10 per cent of that for asphalt.

TABLE II  
THERMAL PROPERTIES OF VARIOUS MATERIALS

Material	$\lambda \left[ \frac{\text{cal}}{\text{cm sec degree}} \right]$	$k (\text{cm}^2/\text{sec})$
Rubber	about $1 \cdot 10^{-3}$	about $2 \cdot 10^{-3}$
Asphalt	about $1 \cdot 10^{-3}$	about $2 \cdot 10^{-3}$
Basalt	about 3 to $4 \cdot 10^{-3}$	about $8 \cdot 10^{-3}$
Iron	about $100 \cdot 10^{-3}$	about $200 \cdot 10^{-3}$

*Rolling tire with little slippage.*—The pattern of frictional work with time in a rotating surface zone of a rolling tire is shown in Figure 10.

During the pulse period  $\tau_p$ , a specific heat current flows according to Equation (27).

$$j = \mu \cdot p \cdot v = \mu \cdot p \cdot \omega \cdot r \cdot S \quad (27)$$

In this equation:

$\omega$  = Rotation frequency

$r$  = Radius of the tire

$S$  = Slippage

For  $\mu$  in Equation (27) we will assume an upper limiting value of 0.9 and for  $p$  we will assume a usual value for tire loading of  $4 \text{ kg/cm}^2$ .

The fraction  $j_1$  of the specific heat current  $j$  flows in Medium 1, in our case the tire, in accordance with Equation (8).

$$j_1 = j \cdot \frac{1}{1 + \sqrt{\frac{k_1 \tau_p}{k_2 \tau_p} \cdot \frac{\lambda_2}{\lambda_1}}} \quad (27a)$$

Since with asphalt as the rubbed base or road material, the expressions  $k_1 = k_2$  and  $\lambda_1 = \lambda_2$  are nearly true,  $j_1 = 0.5j$  and hence the friction temperature is given by Equation (28)

$$T_R = j / 2 \cdot 2 \sqrt{\frac{k_1 \tau_p}{\pi \lambda_1^2}} \quad (28)$$

Taking as an example a rolling tire traveling at 100 km/hr or 30 m/sec and with a slippage of 3 per cent, the pulse period  $\tau_p = 5 \cdot 10^{-3}$  second and we find the specific heat current:

$$j = 0.9 \times 4 \times 30 \times 0.03 \text{ kg/cm}^2\text{sec} \cong 330 \text{ kg cm/cm}^2\text{sec} \cong 8 \text{ cal/cm}^2\text{sec}$$

Equation (28) gives the value for the friction as:

$$T_R = 2 \cdot 4 \sqrt{\frac{2 \cdot 10^{-3} \cdot 5 \cdot 10^{-3}}{3.14 \cdot 10^{-6}}} = 15^\circ \text{ C} \quad (28a)$$

The temperature gradient is localized in a boundary layer about  $6.5 \times 10^{-3}$  cm thick. Here, as in all the following cases, the tire will be considered as having the same temperature  $T_0 = 0$  everywhere when time  $t = 0$ . A warming caused by the periodic passage through the contact zone will be disregarded. Likewise we will assume that the friction temperature dies away again to zero after a revolution.

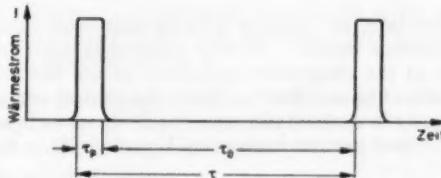


FIG. 10.—The pattern of frictional work with time in the rotating surface zone of a tire.  
Ordinate: Heat current. Abscissa: Time.

**Tire on a curved path.**—If we consider a tire traveling on a curve with a velocity of 50 km/hr, and a side slippage of 10 per cent then analogous calculations give a specific heat current  $j = 13 \text{ cal/cm}^2 \text{ sec}$ , an impulse duration  $\tau_p = 1 \times 10^{-2} \text{ sec}$ , and hence a friction temperature of  $35^\circ \text{ C}$ , which is localized in a boundary layer  $9 \times 10^{-3}$  cm thick.

**Spinning tire.**—Consider as an extreme case a tire which by a momentary extreme acceleration is caused to slip badly. It has a rotation frequency of 10 cycles/sec and a slippage of 50 per cent. These conditions would lead to a specific heat current  $j = 120 \text{ cal/cm}^2 \text{ sec}$ , and  $j_1 = 0.5j = 60 \text{ cal/cm}^2 \text{ sec}$ , with  $\tau_p = 6.5 \times 10^{-3} \text{ sec}$  and a boundary layer  $d_p = 7.0 \times 10^{-3} \text{ cm}$  thick. Then the friction temperature  $T_R$  is:

$$T_R = 60 \cdot \frac{7.0}{\sqrt{\pi}} \cdot 10^{-3} \cdot 10^{+3} = 240^\circ \text{ C} \quad (28b)$$

**Sliding tire.**—As a further extreme case, let us in conclusion consider a locked tire which skids on the highway surface, starting with the initial velocity  $v_0 = 120 \text{ km/hr} = 35 \text{ m/sec}$ . In this case, the initial value of the specific heat current is  $j_0 = 300 \text{ cal/cm}_2 \text{ sec}$ . In the following we have assumed that the specific heat current falls during the braking period in accordance with an exponential function with a time constant  $\tau = 2 \text{ sec}$ . See Equation (29)

$$j = j_0 \cdot e^{-t/\tau} \quad (29)$$

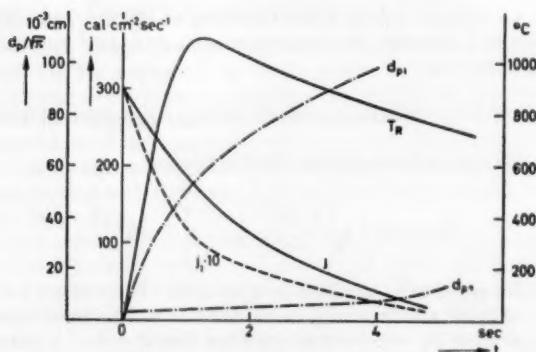


FIG. 11.—Temperature pulse  $T_R(t)$  for a sliding tire. The figure shows the time course of the friction temperature ( $T_R$ ), of the total heat current  $j$  and the component  $j_1$  (the latter on a scale of 10:1) as well as the thickness of the boundary layers,  $d_{p1}$  and  $d_{p2}$ .

Some other function, for instance a linear reduction, does not lead to any fundamentally different results. We felt justified in assuming an exponential function because of the progressive reduction of the friction coefficient as a result of the so called "smear effect". Since the contact surface of the slipping tire comes constantly in contact with new (cool) street surface, the distribution law for the specific heat current is given by Equation (8) in the form:

$$j_1 = j \frac{1}{1 + \sqrt{\frac{k_1 \cdot \tau_{p1}}{k_2 \cdot \tau_{p2}} \cdot \frac{\lambda_1}{\lambda_2}}} \quad (29a)$$

For our special case with  $k_1 = k_2$  and  $\lambda_1 = \lambda_2$  and a pulse period given by Equation (30) a time dependent heat current is defined by Equation (31).

$$\tau_{p2} = \frac{l_0}{v_0} \cdot e^{t/\tau} \quad (30)$$

$$j_1 = j_0 \cdot e^{-t/\tau} \frac{1}{1 + \sqrt{\frac{t}{l_0} v_0 \cdot e^{-t/\tau}}} \quad (31)$$

The course of the friction temperature as a function of time is then given by Equation (32)

$$T_R(t) = \frac{1}{t^x} \int_0^{t^x} j_1(t) dt \cdot \frac{2\sqrt{k_1 t}}{\sqrt{\pi} \cdot \lambda_1} \quad (32)$$

We calculate, for the present,  $t^x$  with the mean value of the heat current,

$$j_1 = \frac{1}{t^x} \int_0^{t^x} j_1(t) dt \quad (32a)$$

The results of the calculation are plotted in Figure 11.

For the extreme case of a sliding locked tire, we get a temperature pulse with a maximum temperature of about  $1100^{\circ}\text{C}$ . This value, as well as all other values calculated above  $200^{\circ}\text{C}$ , is naturally purely fictitious, since at temperatures above  $200^{\circ}\text{C}$ , decomposition of rubber sets in. (For further details, see the following section.)

To conclude this part of the work, the results of the study of the four special cases are brought together in Table III.

#### ABRASION BY THERMAL DECOMPOSITION OF RUBBER

It is evident from the previous section and particularly Table III that abrasion through thermal decomposition should play no part in cases of normal driving. Under extremely severe circumstances, particularly at "contact bridges", very substantial temperature rises may occur. We have ascribed to these cases temperatures (Table III) of  $400^{\circ}\text{C}$  to  $1000^{\circ}\text{C}$  on theoretical grounds, even though we realize that such temperatures for rubber are unrealistic. This is based on the following grounds: it is known that rubber decomposes at temperatures above about  $200^{\circ}\text{C}$ ; the rubber chain molecules are degraded and break apart. Without going into details of the chemical processes involved in this disintegration we wish to make the following assumptions as the bases of further considerations.

1. The thermally disintegrated rubber will be removed from the surface by the rubbing at the moment when it is formed.
2. A definite specific decomposition energy is necessary for the disintegration of the rubber.
3. Decomposed and undecomposed are idealized as two conditions of aggregation of rubber between which there occurs a transition in a temperature interval  $T_s \pm \Delta T^{\circ}$  of the heat current with a time constant  $t \ll$  pulse duration.

If we accept these concepts as the idealization of what really happens, there will be no more temperature rise at the boundary layer between the rubbing bodies after the decomposition temperature  $T_s$  has been reached, but this tem-

TABLE III  
FRICTION TEMPERATURES FOR VARIOUS DRIVING  
CONDITIONS AND ROAD MATERIALS

Friction surfaces Driving conditions	Friction temperature, $^{\circ}\text{C}$						Localization in the bound- ary layer, cm	
	Ideal surface			At "Contact bridges"				
	Asphalt	Basalt Concrete	Iron	Asphalt	Basalt Concrete	Iron		
1. Normal motor vehicle tire, 100 km/hr, slippage = 3%	15	10	2	60	40	8	$6.5 \times 10^{-4}$	
2. Curved road, 50 km/hr, slippage = 10%	35	25	3.5	140	100	15	$9 \times 10^{-4}$	
3. Spinning tire, 10 cycles/sec, slippage = 50%	240	160	24	(1000)	(650)	100	$7 \times 10^{-4}$	
4. Locked skidding tire, max. 120 km/hr starting speed	(1100)	(700)	100			(400)		

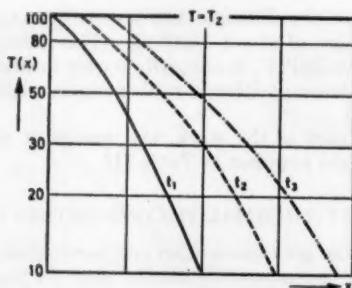


FIG. 12.—Temperature distribution curves. A constant temperature is at once attained in the boundary layer which moves into the medium.

perature will be maintained constant because of the onset of decomposition and the continuous cleaning of the surface.

Now if a heat current  $j_1$  flows in our Medium 1 (rubbing body), then a fraction thereof,  $j_T$ , is necessary, according to Equation (33) to maintain the decomposition temperature, and the fraction  $j_s$  will be needed for the decomposition (see Equation 34). If we assume that an amount of energy  $E_s$  is needed for the thermal decomposition of one gram of rubber, then the energy required to decompose  $m$  grams of rubber is given in Equation (35).

$$T_s = j_T \cdot \frac{dp}{\lambda_1} = j_T \cdot 2\sqrt{\frac{k_1 t}{\pi \lambda_1^2}} \quad (33)$$

$$j_s = j_1 - j_T \quad (34)$$

$$Q = m \cdot E_s \quad (35)$$

at the equilibrium state we have the equation:

$$\frac{\partial Q}{\partial t} = (j_1 - j_T) \cdot F = \frac{dm}{dt} \cdot E_s \quad (35a)$$

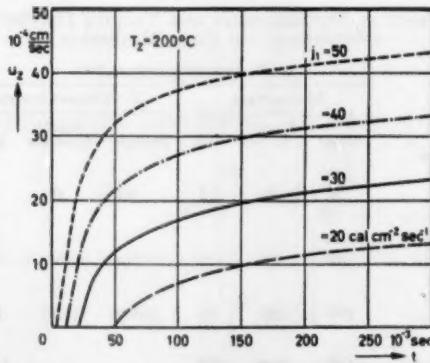


FIG. 13.—Rate of decomposition as a function of time.

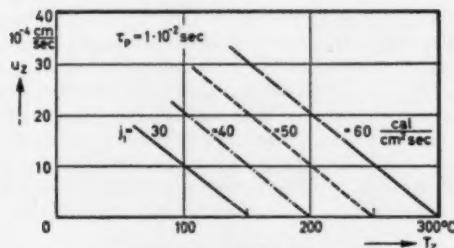


FIG. 14.—Rate of decomposition as a function of the decomposition temperature.

which we may write in the form of Equation (36), using  $m = gV = gFz$ . In this expression  $m$  = mass,  $V$  = volume and  $F$  = area of the contact zone.

$$(j_1 - j_T) = \rho \cdot E_s \cdot \frac{dx}{dt} = \rho \cdot E_s \cdot u_z \quad (36)$$

Thus we can define a rate of decomposition  $U_z = dx/dt$ , as the rate with which the boundary layer moves into our medium. Then curves may be derived for the temperature distribution as shown in Figure 12.

To summarize once more: The specific heat current at the boundary layer, where the fixed decomposition temperature is established, divides into two components; one of which is necessary to provide for the temperature gradient, as in Equation (37), the other of which is needed for the decomposition, as in Equation (38). The decomposition then proceeds in the direction in which the heat current flows in the rubbing medium at a velocity given in Equation (39).

$$j_T = \lambda_1 \cdot \frac{T_z \sqrt{\pi}}{2 \sqrt{k_1 t}} \quad (37)$$

$$j_s = j_1 - \lambda_1 \frac{T_z \sqrt{\pi}}{2 \sqrt{k_1 t}} \quad (38)$$

$$u_z = \frac{j_1 - \lambda_1 \frac{T_z \sqrt{\pi}}{2 \sqrt{k_1 t}}}{\rho \cdot E_s} \quad (39)$$

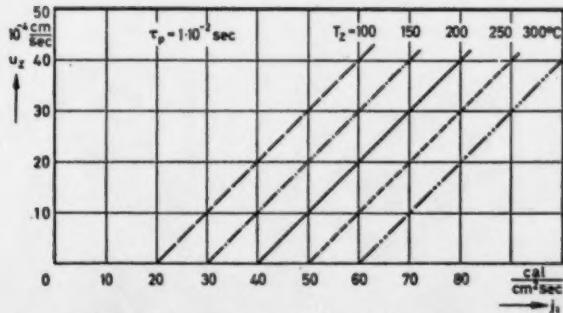


FIG. 15.—Rate of decomposition as a function of the specific heat current.

For the interpretation of Equation (39) we will use the values from Table II for  $\lambda_1$  and  $k_1$  and for the value of the specific decomposition energy  $E_s$ , we will use, as an upper limit, the value for the chemical bond energy for the carbon-carbon linkage. This is given as about 100 kcal/mole or about  $10^4$  cal/g. With these values as the basis for calculations, the curves given in Figures 13, 14, and 15 were derived. In these curves, the decomposition is shown as a function of time, as a function of decomposition temperature, and as a function of the specific heat current. In Figures 14 and 15 a pulse duration  $\tau_p = 1 \times 10^{-2}$  sec is used. This is about the value for a tire rolling at 50 km/hr.

### SUMMARY

In this research, an attempt is made at determining the frictional temperatures which may occur in tires under various driving conditions. This is based on phenomenological theories of heat conduction. Since these temperature pulses are to be traced back to heat current pulses which may last in the neighborhood of  $10^{-2}$  second, the resulting warming will be localized in boundary layers of the order of  $10^{-2}$  cm. From the estimated values of the temperatures, it is concluded that the abrasion which occurs under normal driving conditions is purely mechanical. Only under extreme conditions, such as in very rapid acceleration, or in case of locked wheels—particularly at what we call “contact bridges” or surface elevations—may we expect high frictional temperatures, which lie far above the decomposition temperature of rubber.

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# THE ORGANIC NATURE OF CARBON BLACK SURFACES \*

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## INTRODUCTION

A recent paper by Garten and Weiss<sup>1</sup> has shown that some of the reactions of the surfaces of carbon black particles can be explained as reactions of hydroquinone and quinone structures. Most recently Studebaker, Huffman, Wolfe and Nabors<sup>2</sup> have shown by analysis with diazomethane and other reagents that as much as 18% of the oxygen found on carbon blacks may be present in a 1,4-quinone form. Independently, by the use of infrared and polarographic analyses, the same qualitative conclusions have been reached in these laboratories. These techniques were used to identify functional groups on the carbon black particle surface. On the basis of the presence of these functional groups, a mechanism for the chemical interaction of carbon blacks with elastomers is proposed.

## DISCUSSION OF RESULTS

*Evidence from infrared spectra.*—In general, infrared analyses were unsuccessful, perhaps due to absorption and scattering of the radiation by the particles. However, in the case of a channel black of 8–10  $\mu$  particle diameter and which had a high percentage of chemisorbed oxygen the method proved to be practical. Curve A in Figure 1 shows the infrared spectrum obtained from a Nujol mull of this black.

The band at 6.3  $\mu$  is attributable to either condensed aromatic ring systems or to hydrogen-bonded, conjugated carbonyl groups. Treatment of this black with diazomethane, which would react with groups containing an active hydrogen and thus render these groups incapable of hydrogen bonding, caused a shift of this band to the normal carbonyl wave length of 5.7–5.9  $\mu$  as shown on Curve B in Figure 1.

A very weak band can also be noted on Curve B at about 8  $\mu$  which could conceivably be attributed to aromatic methoxy groups. If this assignment is correct, the band indicates indirectly the presence of aromatic hydroxyl groups, and that the hydrogen bonding to the conjugated carbonyl group was through phenolic hydroxyl groups.

Because infrared analysis was not generally successful, these data could only be taken as indications of what types of groups to look for in other carbon blacks, especially those which did not show an interpretable infrared spectrum.

*Evidence from polarographic analyses.*—In order to determine whether or not carbonyl groups were generally present on carbon black surfaces, as well as the nature of these carbonyl groups, a series of blacks were submitted to polarographic analysis. The initial results apparently were successful, since most of

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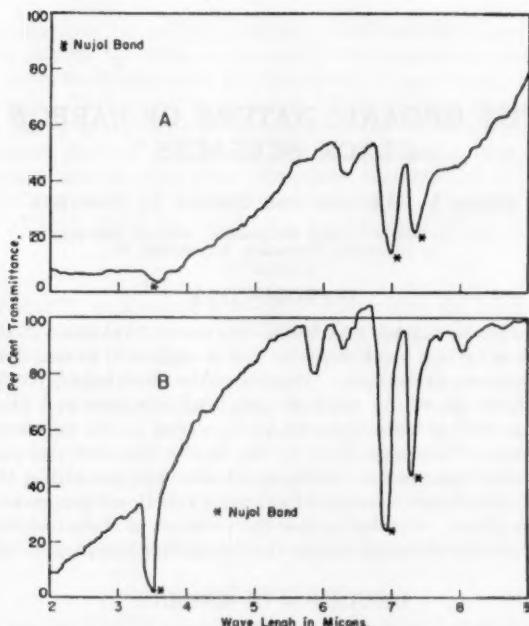


FIG. 1.—A, infrared spectrum of untreated channel black of 8-10 m<sub>p</sub> diameter; B, infrared spectrum of the same black after treatment with diazomethane.

the blacks studied gave a large wave in the range corresponding to quinone reduction as shown in Figure 2. However, three obvious possibilities for misinterpretation had to be eliminated before these results could be accepted. These possibilities were: (1) that the method was intrinsically unsuited for analysis of slurries of blacks; i.e., the customary current-concentration relationship might not be observed; (2) that a reaction between the black surfaces and the supporting electrolyte, tetra-*n*-butylammonium iodide might be occurring to form a product which could then be reduced at the dropping mercury electrode; (3) that the solvent employed, dimethylformamide, might be extracting

TABLE I  
WAVE HEIGHTS AND HALF-WAVE POTENTIALS OF THE SAME ISAF TYPE  
OF FURNACE BLACK IN 0.1 M TETRA-*n*-BUTYLAMMONIUM IODIDE  
IN DIMETHYLFORMAMIDE

Wt of black in 25 ml slurry, g	Wave height ( $\mu$ amp)	$E_{1/2}^b$ (v vs. Hg pool)
1.00	3.2	-0.73
0.50	1.5	-0.68
0.10	0.3	indistinct
1.00*	3.4	-0.69
1.00*	3.6	-0.69

\* Previous runs.

<sup>b</sup> Corrected for ohmic potential.

smaller molecules from the particles which then being in true solution could be available for reduction.

Table I shows the results of varying the concentration of a given furnace black in the same slurry.

Since the height of the wave is directly proportional to the amount of black used, while the half-wave potential remains constant, it is possible to conclude that the polarographic method is not impractical for the analysis of these solids, assuming the other possibilities for error are not operating.

The results of changing the supporting electrolyte in order to eliminate the second possibility of misinterpretation, a reaction between the supporting electrolyte and the black surfaces, is presented in Table II.

The use of a different supporting electrolyte would be expected to cause the wave to be eliminated entirely or to shift radically if it were caused by a reaction of the iodide ion with the carbon black surface. Since, as seen in Table II, no significant shifting occurred beyond the amount expected due to a change in the

TABLE II

EFFECT OF CHANGING THE SUPPORTING ELECTROLYTE ON HALF-WAVE POTENTIALS AND WAVE HEIGHT OBSERVED IN SLURRIES OF THE SAME ISAF BLACK

Slurry of 1.00 g furnace black in 0.1 M	$E_{1/2}^a$ (v vs. Hg pool)	Wave height (amp)
Tetra- <i>n</i> -butylammonium <i>iodide</i>	-0.73	3.2
Tetra- <i>n</i> -butylammonium <i>bromide</i>	-0.79	3.8
Lithium chloride	-0.58	2.9

\* Corrected for ohmic potential.

system, the conclusion is drawn that the electrolyte is not responsible for the observed wave. The higher value shown for the lithium chloride solution is perhaps due to the poorly defined wave obtained with this electrolyte. The wave was not as sharp as in the case of the bromide or iodide solutions.

The time elapsing between mixing the slurries and pouring them into the polarographic cell apparently had no effect on either the height or position of the wave, even when this varied from a few minutes to three days. However, to ensure that dimethylformamide was not extracting reducible materials from the black particles, a sample of a furnace black was extracted with this solvent for one week in a Soxhlet extractor. The extracts were made 0.1 M with respect to the supporting electrolyte and a polarogram was measured. The current-voltage curve obtained was indistinguishable from the residual current curve.

With the elimination of these three possibilities for misinterpretation of the data, it is concluded that the waves observed are due to functional groups on the surface of the carbon black particles.

The polarogram shown in Figure 2 has only one wave. While some of the blacks showed two waves, the general case was for a single wave to appear. At first this would appear to be incongruous with the data obtained by Wawzonek, Berkey, Blaha and Runner<sup>3</sup> on the polarographic analysis of quinones. However, since these quinone carbonyl groups are a part of the surface of a relatively large particle, the second quinone carbonyl, if it exists at all, must be buried

within the bulk of the particles themselves, and thus is not available for reduction as such. However, the valency requirements must be satisfied as will be discussed later. Those blacks exhibiting a second wave (see Table III) could have an additional type of functional group on the surface which need not be related structurally to the quinone types of groups.

A somewhat similar phenomenon has been reported by Micka<sup>4</sup>. An activated carbon was found to depolarize a dropping mercury electrode only in a stirred system. Since in all cases reported in this paper no stirring was used, it is felt that the differences lie either in type of material used by Micka or

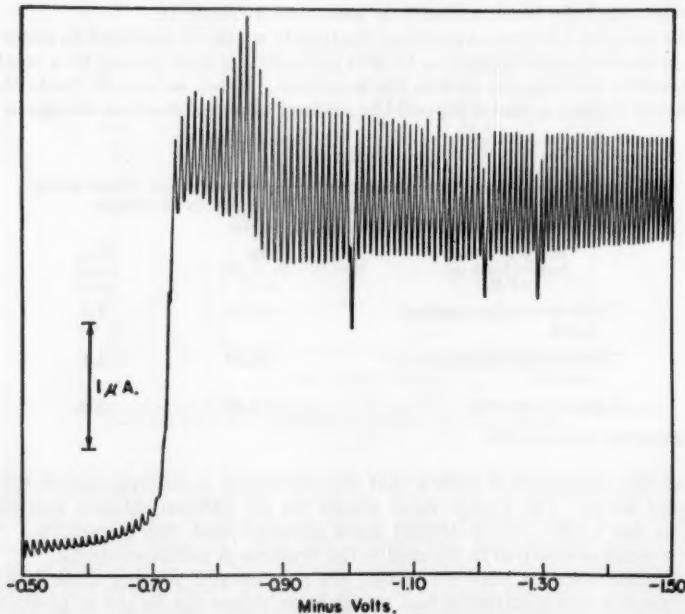


FIG. 2.—A typical polarogram obtained from an ISAF black in dimethylformamide using tetra-*n*-butylammonium iodide as supporting electrolyte.

differences in the solvent action of water and dimethylformamide upon the particles. It is possible that the failure of water to suspend a significant fraction of the particles was overcome by stirring in Micka's experiments.

The results obtained by polarographic analysis of some typical blacks are set forth in Table III.

An analysis was made on the wave occurring between -0.6 and -0.8 v in order to determine the number of electrons involved in the reduction and the nature of the electrode process involved. A plot of  $\log i/(i_d - i)$  vs.  $E$  indicated that two electrons are transferred in the reaction. Wawzonek et al.<sup>4</sup>, found that a two electron reduction of quinone carbonyl groups is to be expected if the carbonyl groups were hydrogen bonded. In the mechanism proposed, the hydrogen would be transferred to the carbanion free radical formed and give a free radical which would reduce immediately.

A plot of  $\log i$  vs.  $\log P$  (where  $P$  represents the mercury pressure in centimeters corrected for back pressure) for the same black gave a slope of 0.44, indicating that the electrode process is predominantly diffusion controlled. A value to this slope of 0.5 would indicate that the process was probably controlled only by diffusion. Deviations of the value of the exponent,  $x$ , in the relationship  $i = kP^x$  from 0.5 were not sufficiently large to suggest that either kinetic or catalytic processes are operative<sup>8</sup>.

For additional evidence that these observed waves were due to quinone reduction, it was considered necessary to cause the wave to disappear by means of suitable chemical treatment of the blacks. The reagents chosen were lithium aluminum hydride and methylmagnesium iodide. Both of these re-

TABLE III

HALF-WAVE POTENTIALS AND WAVE HEIGHTS OBSERVED IN SLURRIES OF TYPICAL CARBON BLACKS IN 0.1 M TETRA-*n*-BUTYLAMMONIUM IODIDE IN DIMETHYLFORMAMIDE

Type of black <sup>b</sup> (1.00 g)	$E_{1/2}^a$ (v vs. Hg pool)	Wave height (amp)
1. ISAF	-0.76	3.3
2. ISAF	-.73	3.2
3. ISAF	-.71	2.8
4. ISAF	-.77	2.7
5. SAF	-.82	2.8
6. ISAF	-.75	3.3
7. FF	-1.54	6.4
8. ISAF	-1.56	1.5
9. ISAF	-0.77, -1.69	2.0, 0.6
10. High color black	-.78	127.0
11. Lamp black	-.57	1.6
12. Intermediate color black (Channel)	-.62, -1.43	56.0, 23.0

<sup>a</sup> Corrected for ohmic potential.

<sup>b</sup> The designations used throughout this paper are standard rubber industry classifications of carbons. These designations usually refer to the intended uses of the final rubber stock, although the method of manufacture is sometimes implied. For example, ISAF means intermediate super abrasion furnace; SAF, semi-abrasion furnace; FF, fine furnace; HAF, high abrasion furnace; MPC, medium process channel; FT, fine thermal; HMF, high modulus furnace; EPC, easy process channel.

agents reacted vigorously with the blacks studied. In both cases the treatment resulted in the complete disappearance of the wave, indicating that the reagents had converted the quinone groups to groups not reducible in this potential range (-0.6 to -0.8 v).

Not all the blacks studied gave a wave in the region of quinone reduction. Several blacks (see Table III) showed waves in the region -1.54 to -1.63 v. It is possible that this wave is due to the reduction of carboxyl groups. However, this possibility has not been investigated as yet.

An analysis of the wave occurring in the area of -1.5 to -1.6 v was carried out in the same manner as for the wave previously discussed. The plot of  $\log i/(i_d - i)$  vs.  $E$  suggested that in this case, the reaction was irreversible, the value  $\alpha(n_a)$  being 0.84. The electrode process involved in this wave was likewise shown to be largely diffusion controlled since a plot of  $\log i$  vs.  $\log P$  had a slope of 0.41.

A large number of the blacks studied either gave no wave at all or gave a maximum which was, interestingly enough, in the range -0.6 to -0.8 v. At the present time, no sound explanation can be advanced for this phenomenon. However, the possibilities that the presence of hydroquinone groups might

TABLE IV

DESCRIPTION OF POLAROGRAMS OF SOME TYPICAL CARBON BLACKS WHICH DID NOT EXHIBIT A WAVE ON POLAROGRAPHIC ANALYSES

Type of black (1.00 g)	Position of max. (v vs. Hg pool)	Height of max. (amp)
1. ISAF	-0.67 (maximum)	1.2
2. ISAF	- .86 (maximum)	2.6
3. ISAF	- .73 (maximum)	1.5
4. HAF	- .74 (maximum)	1.5
5. HAF	No wave or maximum	
6. HMF	No wave or maximum	
7. LiAlH <sub>4</sub> treated ISAF <sup>a</sup>	No wave or maximum	
8. LiAlH <sub>4</sub> treated MPC <sup>a</sup>	No wave or maximum	
9. Grignard treated MPC <sup>a</sup>	No wave or maximum	
10. FT	No wave or maximum	

<sup>a</sup> Each of these carbon blacks had shown a wave in the region -0.6 to -0.8 v before the indicated treatment.

affect the polarographic behavior of quinones as a result of hydrogen bonding, or that a competing reaction may be occurring at the mercury pool are being investigated. Some typical blacks which display this type of behavior are listed in Table IV.

Since the few interpretable infrared spectra obtained indicated the possibility of the presence of phenolic groups on the surface, it was hoped that anodic polarography could be used to establish this group in the same manner with which quinone groups were studied with cathodic polarography. Practically all of the blacks examined gave a wave at about +1.00 v. This wave disappears upon treatment with hydrogen peroxide or diazomethane. Both this wave, which is assumed to be due to a hydroquinone group, and the quinone wave disappear upon heating the blacks to temperatures of 1950°. Table V lists some typical results from polarograms measured in a sodium nitrate solution (0.1 M) in dimethylformamide.

TABLE V

HALF-WAVE POTENTIALS AND WAVE HEIGHTS OF SLURRIES OF SOME TYPICAL CARBON BLACKS IN 0.1 M SODIUM NITRATE IN DIMETHYLFORMAMIDE USING A PLATINUM ELECTRODE

Type of black (1.00 g)	$E_{1/2}$ (v vs. SCE)	Wave height (amp)
1. ISAF <sup>a</sup>	+0.96	9.2
2. ISAF <sup>a</sup>	+ .95	10.5
3. ISAF <sup>a</sup>	+ .97	11.0
4. ISAF <sup>a</sup>	+ .96	10.0
5. ISAF <sup>a</sup>	+ .95	11.5
6. ISAF <sup>a</sup>	+ .97	16.0
7. ISAF	+ .95	9.0
8. EPC	+1.02	3.0
9. EPC	+1.02	3.0
10. High Color	+0.88	19.0
11. HAF	+1.05	7.2
12. SAF	+0.98	4.0

<sup>a</sup> Experimental carbon blacks in the fineness range of ISAF.

## MODEL CARBON BLACK PARTICLE

For convenience in presenting a mechanism for the interaction of carbon black and elastomers based on the functional groups indicated by the preceding data, the model carbon black particles as shown in Figure 3 is first constructed. As described by Biscoe and Warren<sup>6</sup>, the internal portions of the particles are occupied chiefly by graphitic crystallites. It is proposed that the hydroxyl and quinone groups occur on the edges of aromatic rings of these crystallites which occasionally jut out from the average surface of the particle. Hydrogen-bonding could then be established from a hydroxyl group to a quinone group whether the functionalities are on the same plane of a crystallite or an adjacent plane. The distance is too great in the case of adjacent planes (usually about 3.55 Å) to permit hydrogen-bonding in its most effective form, but the hydrogen atom in the hydroxyl group would undoubtedly be rendered more acidic than normal.

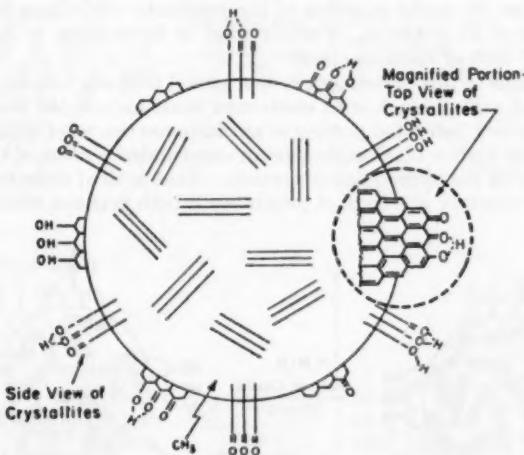


FIG. 3.—Model of carbon black particle.

## INTERACTION OF CARBON BLACK WITH ELASTOMERS

Before a scheme for the interaction of carbon blacks with elastomers could be proposed, it was considered necessary to determine whether or not the presence of these functional groups was a mere triviality. To test this possibility, a furnace black in wide use in the rubber industry was chosen which had both quinone and hydroquinone waves. In one case, this furnace black was treated with gaseous peroxide-free butadiene. Upon polarographic analysis, it was observed that while the quinone wave had not been affected in any way, the hydroquinone wave had completely disappeared. In a second case, the same black was heated to reflux temperature in 2,2,4-trimethylpentane (b.p. 99.3°); the quinone wave disappeared while the hydroquinone wave remained unchanged. These results are summarized in Table VI.

That this type of reaction is possible was shown by heating benzoquinone itself under reflux with 2,2,4-trimethylpentane for three days. After removal of the solvent at reduced pressure to prevent decomposition of the benzoquin-

TABLE VI

WAVE HEIGHTS AND HALF-WAVE POTENTIALS OF A CARBON BLACK AFTER TREATMENTS WITH SATURATED AND UNSATURATED HYDROCARBONS

ISAF type carbon black (1.00 g)	$E_{\frac{1}{2}}$ (v vs. Hg pool)	Wave height (amp)	$E_{\frac{1}{2}}$ (v vs. SCE)	Wave height (amp)
Untreated	-0.72	2.80	+1.02	8.0
Treated with butadiene	-0.72	2.80	No wave	—
Treated with 2,2,4-trimethyl pentane	No wave	—	+1.02	8.0

one, a polarogram was run on the residue. This polarogram clearly showed the presence of an oxidizable group in that a wave was observed at +0.66 v. This wave could not be found in either of the reactants, while pure hydroquinone showed a wave at +0.62 v. Further work is in progress to determine the generality of both of these reactions.

On the basis of this experiment it is proposed that any scheme for the total interaction of carbon black with elastomers must include the possibility that either a branched, saturated portion of an elastomer can react with the quinone portions of the carbon black surface or an unsaturated portion of the elastomer could react with the hydroquinone portion. That both of these routes may be taken simultaneously is a distinct possibility if both types of sites occur in the

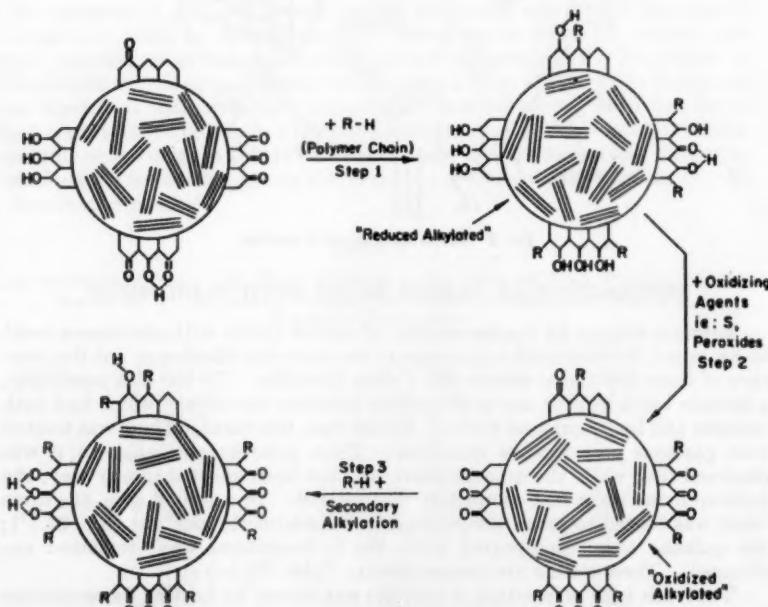


FIG. 4.—Mechanism A: proposed scheme for the interaction of carbon blacks with saturated molecules.

elastomer and both quinones and hydroquinones exist on the carbon black surface.

The following two reaction schemes are proposed to account for the total interaction of carbon black and elastomers.

Figure 4 shows the proposed mechanism for the reaction of branched, saturated molecules with carbon black. This scheme, Mechanism A, is described using a simplified version of the model in Figure 3 as the quinone. Mechanism A is composed of three distinct steps, although all three of them may be occurring simultaneously at different portions of the particle. The

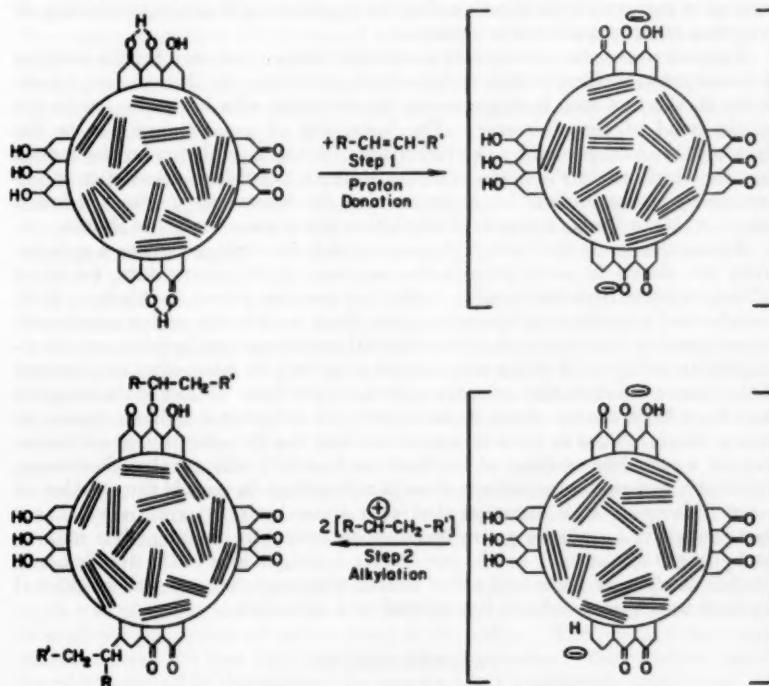


FIG. 5.—Mechanism B: proposed scheme for the interaction of carbon blacks with unsaturated molecules.

first step depends upon the ability of the quinone group to abstract a hydrogen from the saturated chain. This would undoubtedly take place on the most highly substituted carbon atoms from which the hydrogen atoms are more easily abstractable. In this process, the quinone groups are reduced to hydroquinones and the aromatic rings are attacked by the radical resulting from the removal of a hydrogen from the chain. The product obtained as a result of this first step is referred to as the "reduced, alkylated," particle. This reduced, alkylated particle is perhaps similar to the "benzene insoluble gel" described by Sweitzer, Goodrich and Burgess<sup>7</sup>.

Obviously, the hydroquinone groups could not enter into this type of a reaction scheme since they are already in a reduced form and thus are incapable

of removing a hydrogen from the chain. However, in the presence of oxidizing agents such as sulfur or peroxides these functionalities can be converted into quinone groups for further reaction as shown in Step 2 with the formation of the "oxidized, alkylated" particle.

This oxidized, alkylated particle can then participate in a secondary alkylation according to Step 3 to give the fully alkylated particle. This step is identical to Step 1. The entire series could be repeated over and over again as long as alkylatable sites exist or as long as the oxidizing agent persists in a useful form in the neighborhood of the reaction. Even after all of the oxidizing agent is used up or removed from effective sites the reaction could proceed following air oxidation of hydroquinones to quinones.

Figure 5 shows the corresponding reaction scheme proposed for the reaction of unsaturated molecules with carbon black particles. In this scheme, Mechanism B, the first step is suggested as the donation of a hydrogen ion to the double bond of the elastomer. The formation of a carbonium ion in the elastomer is accompanied by the formation of a negative charge on the carbon particle which could shift into the ring if at all possible. Alkylation of the particle by the carbonium ion is proposed as the second step. Since it is not known whether C-alkylation or O-alkylation takes place, both are shown.

Notice that, only the hydroxyl groups which are written next to a quinone group are shown to participate in the reaction. Preliminary data, taken on rubber, indicate that this is so<sup>8</sup>. In the few samples tested at this date, both modulus and amount of gel decrease, if the black used in the rubber compounding mixture has been reduced, either with lithium aluminum hydride or methylmagnesium iodide. Modulus and amount of gel may be interpreted as measures of the degree of interaction of carbon black with rubber. Both of the reagents used have been shown above to be capable of reducing a quinone group on carbon black. Thus it must be concluded that the quinone groups are necessary for a complete reaction of the black surface with unsaturated elastomers, and that a hydroquinone surface alone is not enough to permit the reaction to occur. However, it is assumed that only those hydroxyl groups which are near enough to a quinone group to establish hydrogen bonding, thus making the hydrogen atoms more acidic, can donate hydrogen ions to the double bond. Further studies on these and other rubber property changes with additional blacks is in progress and will be reported at a later date.

## EXPERIMENTAL

*Infrared analyses.*—The infrared analyses were carried out using a Nujol mull of the black under investigation. A Baird model A infrared spectrophotometer with rock salt optics was used throughout.

*Polarographic analyses.*—For measuring reduction potentials, the slurries were prepared by placing 1.00 g of a carbon black in a 25-ml volumetric flask and diluting to the mark with a solution of N,N-dimethylformamide made 0.1 M with respect to the supporting electrolyte. Tetra-*n*-butylammonium iodide, tetra-*n*-butylammonium bromide and lithium chloride were used as supporting electrolytes. After shaking, the slurry was poured into a polarographic cell and the oxygen removed by bubbling high-purity, dry nitrogen through the slurry for 20 minutes. For measuring oxidation potentials, 0.1 M sodium nitrate in dimethylformamide was used. The polarograms were taken on a Leeds and Northrup Electrochemograph, Type E, using a dropping mercury electrode or a platinum electrode in the case of anodic polarograms. A mer-

cury pool electrode was used as a reference electrode for cathodic polarograms and a saturated calomel electrode for anodic polarograms.

For the capillary used,  $t = 2.72$  sec and  $m = 2.895 \text{ mg sec}^{-1}$  yielding a value of  $2.400 \text{ mg}^{2/3} \text{ sec}^{-1/2}$  for  $m^{2/3}t^{1/6}$ . These values were determined for the electrode immersed in the solvent-electrolyte described above with the electrical circuit open. The dimensions of the platinum wire electrode were: area =  $0.138 \text{ cm}^2$ , radius =  $0.0314 \text{ cm}$ . This platinum electrode was mounted vertically, and a small glass bead was sealed onto the tip to reduce end effects.

*Grignard treatment of the blacks.*—Methylmagnesium iodide was prepared in the usual manner and added dropwise to a stirred slurry of the black in ether. The vigorous reaction which ensued was controlled by the application of an ice bath. After all of the reagent had been added, the mixture was stirred at room temperature for two hours and then heated under reflux overnight. Subsequent heating to reflux temperature for an additional two hours completed the treatment. The excess Grignard reagent was decomposed by treatment with a solution of ammonium chloride. The black was collected on a filter and washed thereon with distilled water. The black was then re-slurried in distilled water with high speed stirring and filtered. This process was repeated three times. The black was then stirred with methyl alcohol, collected on a filter and washed again with methyl alcohol. After drying in air, the treated black was dried overnight in a vacuum oven at  $70^\circ$ .

The preparation of a control black was carried out using every step in the above except the addition of methylmagnesium iodide solution.

*Treatment of blacks with diazomethane.*—An ether solution of N-methyl-N-nitroso-p-toluenesulfonamide was treated with 0.015 mole of cold alcoholic potassium hydroxide<sup>9</sup> and the resulting solution distilled on a steam-bath directly into a test-tube containing the carbon black covered with dry ether and cooled in an ice-bath. The distillation was continued as long as a yellow color persisted in the distillate. The yellow color persisted for about two hours in the solution over the carbon black. After the color had disappeared, the ether was evaporated and the black was dried overnight in a vacuum oven at  $70^\circ$ .

The control black was prepared by evaporating ether from a sample of the carbon black.

*Lithium aluminum hydride treatment of blacks.*—Lithium aluminum hydride was placed in the thimble of a Soxhlet extractor and added continuously to a stirred suspension of carbon black in dry ether. The reaction was rather violent during the first few deliveries of the extractor. The reaction was allowed to proceed in this manner for one week. Considerable amounts of lithium aluminum hydride remained in excess. This was decomposed by the addition of wet ether. The treated black was collected on a filter and washed with ether. The black was then re-slurried in distilled water with high speed stirring and filtered. This process was repeated three times. The black was then stirred with methyl alcohol, filtered, washed again with methyl alcohol and dried in air. After drying overnight in a vacuum oven at  $70^\circ$ , the treatment was complete.

The control black was prepared by heating the black to reflux for the same length of time as above and washing and drying in an identical manner.

*Butadiene treatment.*—This work is a part of an unpublished study carried on in the laboratories of Columbian Carbon Company, New York. The method consists of passing butadiene onto carbon black contained in the bulbs of a nitrogen adsorption apparatus. The difference between the measured volume of butadiene added to the sample and that desorbed by pumping the

sample while heated by boiling water is taken as the volume of butadiene which reacted with the carbon black. The results of this study will be reported in a later paper.

#### SUMMARY

Evidence is presented for the existence of quinone groups and aromatic hydroxyl groups on the surface of carbon black particles. This evidence is based largely upon polarographic analyses of slurries of carbon blacks. A mechanism for the chemical interaction of carbon blacks with elastomers is proposed on the basis of these functional groups.

#### ACKNOWLEDGMENT

This investigation was supported by the Columbian Carbon Company. The infrared spectroscopy was done in the laboratory of Dr. Foil A. Miller. The rubber measurements and the butadiene adsorption was done in the laboratories of the Columbian Carbon Company.

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## ANALYSIS OF ACCELERATORS AND ANTIOXIDANTS \*

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For many years the identification of accelerators and antioxidants in vulcanized rubbers was attempted by the application of color reactions directly to the solvent extract of the rubber. Unfortunately very few of the reactions were specific for one compound and they were frequently masked by other colored compounds in the extract. The problem is, of course, complicated by the fact that the compounds appearing in the solvent extract from the vulcanized rubber are not necessarily those which are added to the original mix. The accelerators in particular are liable to undergo considerable decomposition during vulcanization. At first sight the ultraviolet absorption spectrum of the extract might be expected to give the necessary information. The ultraviolet absorption spectra of some of the compounds are reasonably characteristic (Figure 1) but in the extract from the rubber the ultraviolet absorption from the other ingredients (e.g., pine tar) is nearly always sufficient to mask that due to the accelerator or antioxidant. It is usually not possible even to identify the pres-

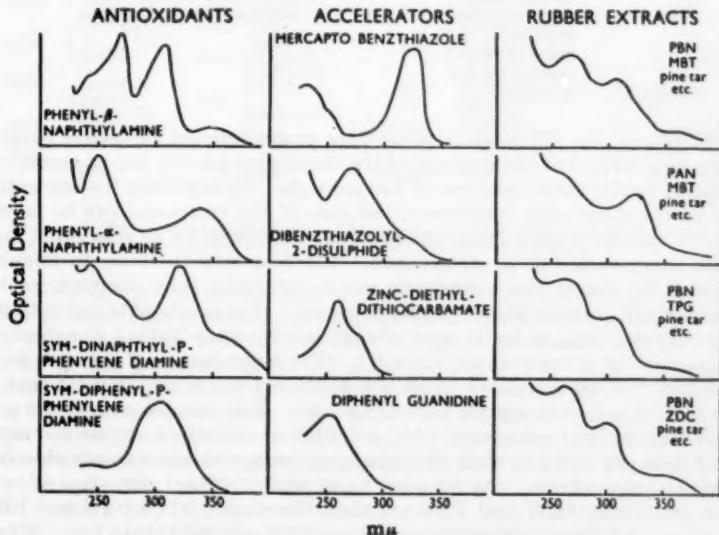


FIG. 1.—Ultraviolet absorption spectra of some antioxidants and accelerators.

\* Summary of a lecture delivered at a joint meeting of the Mid-Southern Counties Section and the Institution of the Rubber Industry at Southampton on 1 March, 1957. Reprinted from the *Journal of the Royal Institute of Chemistry*, Vol. 81, pages 674-679 (1957).

ence of a particular compound, let alone determine its concentration. A selective method of separation of these compounds must be applied before the ultraviolet absorption method can be used. Direct identification is however possible in some cases by other methods. For example recent work<sup>1</sup> has shown that certain constituents of a rubber extract can be identified and quantitatively determined by spectrofluorimetry without separation from the other constituents. This very useful technique is of course only applicable to those constituents which fluoresce.

For the separation of the accelerators and antioxidants prior to ultraviolet absorption measurement, column chromatography on fine silica gel has been used with great success. The advantages of this adsorbent over the more generally used alumina have been discussed in previous publications<sup>2,3</sup>. Some of the main advantages are (*a*) the ease of packing and extrusion of the columns, (*b*) stability of adsorbates which can be recovered quantitatively, (*c*) the high-degree of selectivity which can be attained by the use of binary solvent mixtures and (*d*) low cost.

By experience with many types of organic compound it had been found that the common volatile solvents can be placed roughly in order of 'eluting power,' which is also roughly in order of polarity:

	Eluting power	Some useful binary mixtures
(weakest)	light petroleum (40–50° C) carbon tetrachloride benzene methylene chloride chloroform diethyl ether ethyl acetate acetone ethyl alcohol methyl alcohol pyridine	benzene in light petroleum benzene in $\text{CCl}_4$ ethyl acetate in light petroleum ethyl acetate in $\text{CCl}_4$ ethyl ether in benzene ethyl acetate in benzene
(strongest)		

In general the difference in developing power between successive pairs of solvents is large, but the strength of the developing solvent can be accurately adjusted by the use of mixtures of two solvents. By adjusting the concentration of the more polar constituent, the zone of any compound can be moved into the middle of the column, and optimum conditions for its separation from other compounds can be determined. The first step therefore in devising methods for the various compounds was to determine their chromatographic behavior with various binary solvent mixtures. The results obtained with the four mixtures found to be the most effective are shown in Table I (for chemical composition of compounds see Table II). The concentration of the more polar constituent of the developer which will produce a convenient development of the zone is indicated against each compound. For example with 1 per cent ethyl ether in light petroleum, PAN and PBN are nicely developed and separated from one another, while the remaining compounds are strongly absorbed further up the column. On the other hand, with 10–20 per cent ethyl ether in light petroleum, MBT and TET are nicely developed. The PAN and PBN are eluted and the remaining compounds are still firmly held at the top. Where compounds are not completely separated by one binary mixture, a good separation can usually be obtained by the use of a different one. For example, with mixtures of ethyl acetate and benzene the zone of TMT overlaps that of MBT,

but with ethyl ether in light petroleum the two compounds can be cleanly separated. On the other hand the position is reversed for TC and TMT.

With such chromatographic data as a guide, it was a fairly simple matter to devise a series of columns on one of which every one of the simple compounds considered could be separated cleanly. Although the zones of other more complex mixed accelerators and antioxidants overlapped in many cases, it was so arranged that overlapping zones gave reactions with different streak reagents and so could readily be distinguished from one another. Complete schemes for the separation of these and other commonly used accelerators and antioxidants have been reported previously<sup>3,4</sup>.

TABLE I  
ADSORPTION SERIES OF SOME SIMPLE ACCELERATORS AND  
ANTIOXIDANTS FROM FOUR BINARY DEVELOPERS

(These data apply when the compounds are placed on the column in methylene chloride; some of those compounds giving diffuse zones under these conditions give tight zones when placed in carbon tetrachloride, e.g., Agerite White.)

Benzene/light petroleum	Ethyl ether/light petroleum	Ethyl acetate/benzene	Ethyl acetate/carbon tetrachloride
Strongly adsorbed	DOTG 100% { DPG (a) TPG 50% MTD TPG (b)	Strongly adsorbed { DOTG 20% DPG TPG (b)	Strongly adsorbed { DOTG 50% DPG TPG (b)
	MS 40% { TMT 30% { TC MS	TC MS	MS TC
100% (slightly developed)	TMT MBT 20% { TET (b)	1% { TMT MBT 2% { MBTS	TMT 2% { MBT 2% { TET
100%	TET (b)		
100%	MBTS 10% { Agerite White (b) DPPD (b)	1% { TET Santocure	Santocure
100%	Santocure Agerite White (b) DPPD (b)	0% { Santocure Agerite White (c)	MBTS Agerite White (b) DPPD (b)
30%	DPPD (b)	Eluted DPPD	PBN
15%	PBN 1% { PAN	Eluted PAN	PBN 0% { PAN (mainly eluted with 25 ml)

Notes.—(a) Diffuse zone at top of column. (b) Formation of a very diffuse zone covering a large proportion of the column. (c) Mainly eluted but a pink color remains on column.

All the compounds are colorless and so invisible during development. The silica gel adsorbent is sufficiently reproducible in characteristics, so that once the chromatographic behaviors of the compounds are known it is necessary merely to run a predetermined volume of developer (e.g., 25 ml) through a column of standard size for the zones to appear in the correct places. However, if a further check is required, small quantities of colored compounds may be added to the extract before chromatography. The movement of the indicator zones corresponding to these substances can be used to follow the progress of the development<sup>5</sup>. After development the column is extruded and streaked with various reagents which will produce colors with the compounds being looked for. A wide variety of colorimetric reagents for accelerators and antioxidants are known and from these some appropriate ones were chosen as being sufficiently selective<sup>6</sup>. Thus, with any particular compound the position of the zone, on each of the seven columns, coupled with the colors of the streaks ob-

tained with various reagents, gives an almost unambiguous identification of the accelerator or antioxidant. If further proof is needed or if a precise quantitative result is required, the chromatography is carried out on a 2 cm column, and by careful streaking the zone can be cut out, the streaked portion removed with only slight loss and the remainder eluted with a suitable solvent and its ultra-violet absorption spectrum measured.

TABLE II

COMPOUND ADDED TO RUBBER MIX	WHETHER DETECTED IN UNVULCANISED RUBBER	OTHER COMPOUNDS DETECTED IN VULCANISED RUBBER	COMPOUND ADDED TO RUBBER MIX	WHETHER DETECTED IN VULCANISED RUBBER
<b>THIOPOLYS ETC.</b>			<b>QUATERNIARIES</b>	
	YES	MBTS		
	YES	MBT		
	YES	MBT, MBTS		
	NO			
<b>THIURAMS</b>			<b>OTHER AMINES</b>	
	NO	ZMC (DETECTED AS (A) COMPOUND)		
	NO	ZMC (—→)		
	NO	ZDC (—→)		
<b>THIOCARBAMATES</b>			  ALDOL - NAPHTHYLARINE CONDENSATION PRODUCT FORMALDEHYDE ANILINE CONDENSATION PRODUCT	
	YES (DETECTED AS (A) COMPOUND)			
	YES	(—→)		
			  TOMER I TOMER II	

It so happens that some antioxidants are strongly fluorescent when excited with ultra-violet light, and this method thus provides a very convenient means of following the development of the chromatogram. It must be borne in mind that small quantities of very strongly fluorescent impurity can sometimes be mistaken for a major constituent, and it is necessary to confirm the identity of a fluorescent zone by extrusion of the column and application of the streak reagent. Alternatively the fluorescence spectrum of the zone can be examined during development by observations with a spectrofluorimeter. Spectrofluorimetry is also a very useful method for the quantitative determination of the material after elution. It is much more sensitive than absorption spectrometry.

A rather different method has been used for the separation and identification of the dithiocarbamates. These are of interest for two reasons—first because they are often added to the rubber mix (as their zinc or amine salts) and second because they are formed from other accelerators during vulcanization. For their separation the extract of the rubber in carbon tetrachloride or benzene was shaken with dilute aqueous copper sulfate solution. By this means the dithiocarbamates were converted to their brown copper complexes, which dissolved in the organic layer and could be easily chromatographed. By this means the copper salts of methyl, ethyl, *n*-propyl, *isopropyl*, *n*-butyl and pentamethylene dithiocarbamates could be separated from one another<sup>4</sup>.

The results of the application of the various methods to some vulcanized rubbers are shown in Table II. All the amine antioxidants, with the exception of MTD and MA, were readily detectable after vulcanization. Similarly with the guanidines and the dithiocarbamates. None of the thiurams remained but all were at least partly converted to the corresponding dithiocarbamates during vulcanization. The three thiazoles are interesting. Whether one initially adds MBT or MBTS to the rubber mix, the vulcanized rubber is found to contain both. They apparently come to equilibrium with one another during vulcanization.

A detailed discussion of the results of other workers who have used chromatography for the separation of rubber ingredients is not possible here. Earlier work was carried out by Bellamy, Lawrie and Press<sup>5</sup> and by Mann<sup>7</sup>, all of whom used alumina as adsorbent. More recent work has been reported by Zijp in Holland<sup>8</sup> who has applied paper chromatography after chemical treatment for the identification of a wide variety of accelerators and antioxidants.

In conclusion it should be mentioned that the methods just described were originally developed for the rapid semi-quantitative analyses of large numbers of rubbers. They have been in use, with minor modifications, for more than five years and have proved to be very satisfactory, the combination of chromatographic zone position and streak tests providing a sufficiently unambiguous identification. Occasionally, precise quantitative data have been required, and these have been obtained by separation followed by ultra-violet absorption measurement. It will be realized however that, particularly with the accelerators, it is not always possible to identify the specific accelerator originally added to the rubber because of the transformations it has suffered during vulcanization. In fact the complex chemical reactions in which the accelerator takes part during vulcanization are still not clearly understood. In any investigation of these reactions chromatography on silica gel would undoubtedly provide a very useful method of attack.

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## ERRATUM

### DETERMINATION OF DEGREE OF CROSSLINKING IN NATURAL RUBBER VULCANIZATES. PART II.

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This paper, which appeared in RUBBER CHEMISTRY AND TECHNOLOGY, Volume 30, 11 (1957), contained the erroneous expression  $\frac{1}{4} M_c$  several times throughout the paper. The correct expression is  $1/2 M_c$  which appears in Table III and throughout the paper as originally published in the *Journal of Polymer Science*.

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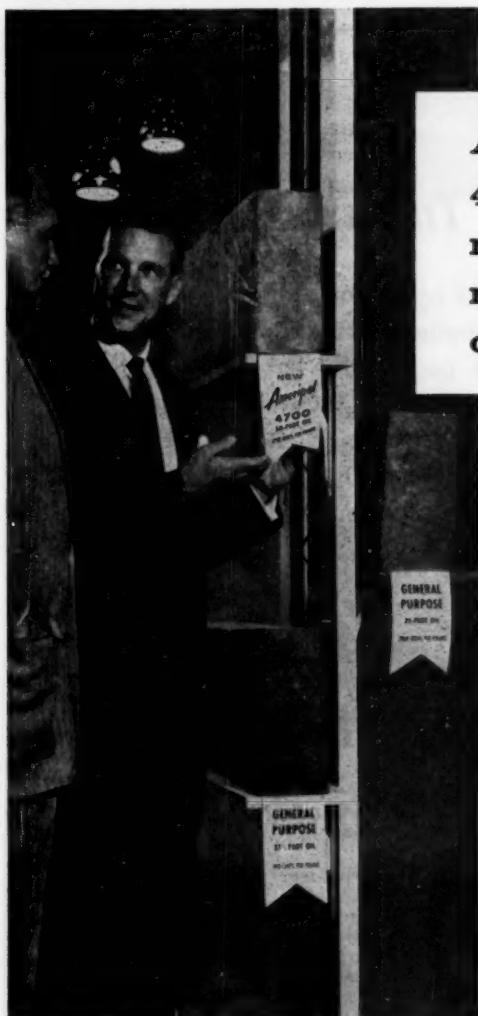


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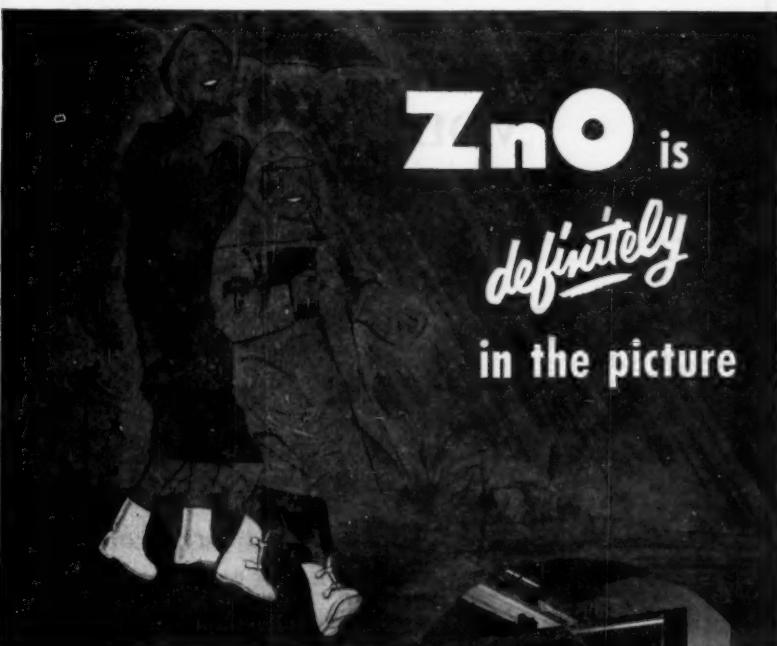
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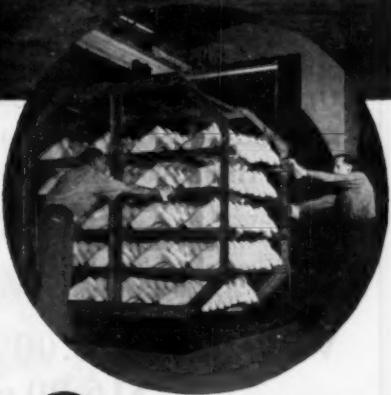
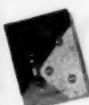
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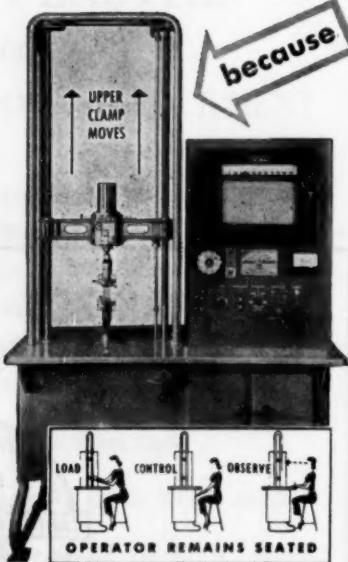
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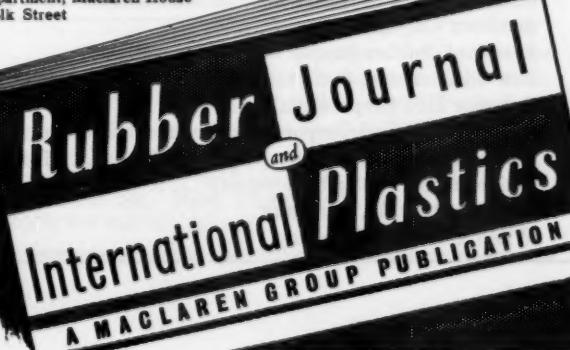
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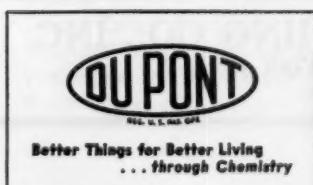
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